JPRS-UCH-92-002
14 FEBRUARY 1992

FOREIGN
BROADCAST
INFORMATION
SERVICE

JPRS Report

Science & Technology

Central Eurasia: Chemistry

19980114 171
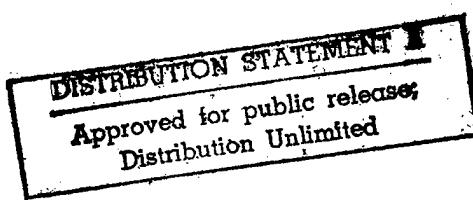
Science & Technology
CENTRAL EURASIA: Chemistry

CONTENTS

CHEMICAL INDUSTRY

COMBUSTION & EXPLOSIVES

INORGANIC COMPOUNDS

ORGANOPHOSPHOROUS COMPOUNDS

PETROLEUM AND COAL PROCESSING

POLYMERS AND RUBBER

RADIATION CHEMISTRY

Industrial Mastering of Direct Ethylene Chlorination Reactor Integrated With Rectification Column

[Article by M. G. Avetyan, E. V. Sonin, O. A. Zaydan et al.]

UDC [66.094.403:661.715.332].002.237

[Abstract] A new procedure for direct chlorination of ethylene was described and discussed. The procedure involved creation of a reactor unified into a single assembly with a 1,2-dichloroethane [DKhE] rectification column which is connected with a column for separation of high-boiling admixtures. Rectification in the unified aggregate is realized because of the heat of reaction. The new technology was tested on an experimental-industrial device with a capacity of 15,000 tons of DKhE per annum at Sayansk industrial association "Khimprom". Data obtained confirmed the promising future of use of this new technology. It made it possible to use the heat of reaction for rectification of both synthesized and extraneous DKhE with an increase of DKhE-rectified spirit almost three times greater than the yield of synthesized DKhE. The expenditure of extraneous vapor consumed, determined by the reflux number, equalled zero in an optimal regime. The DKhE-rectified spirit obtained in the process was very high quality which improves operation of other stages of vinylchloride production. Use of the process almost doubled the reduction of waste waters. Figures 4; references 5 (Russian).

Effect of Technological Regime of Industrial 1,2-dichloroethane Pyrolysis Device on Quality of Vinylchloride

[Article by N. V. Lashmanova, V. A. Kolesnikov, et al.]

UDC [661.7:547.322.32]002.237

[Abstract] A study of the effect of the temperature of pyrolysis, parameters of the technological regime of the hardening system, the presence of admixtures in the 1,2-dichloroethane [DKhE] entering into the pyrolysis reactor and other factors on the butadiene content in vinylchloride was performed on an industrial DKhE pyrolysis device at Dserzhinskiy industrial association "Kaprolaktam". In order to study the effect of the temperature of pyrolysis on the butadiene level in the product, temperature at the pyrolysis furnace outlet was varied from 505 degrees to 490 degrees C. A decrease of temperature at the pyrolysis furnace outlet by 15 degrees decreased the degree of DKhE conversion by 9 percent and the fraction of total mass of butadiene by about $4 \times 10_{-4}$ percent. The effect of admixtures of chlorohydrocarbons in DKhE entering into the pyrolysis reactor on the butadiene content in vinylchloride was determined. Reduction of the temperature of pyrolysis decreased the total volume of admixtures in DKhE entering the pyrolysis reactor from 0.45 percent at 505 degrees C to 0.26 percent at 490 degrees C. Cooling the quenching mixture by 5-10 degrees C increased the quantity of quenching mixture from 26 to 32 t/hr which decreased the temperature in the quenching piece by about 15 degrees C, helped to decrease the admixture level in the quenching mixture and thus decreased the percent of butadienne in the vinylchloride. References 5 (Russian).

Regularities of Course of Accidents at Tanks With Liquified Hydrocarbon Gases With Formation of "Fire Balls"

[Article by A. P. Shevchuk, O. A. Simonov, Yu. N. Shebeko and R. Z. Fakhrislamov]

UDC 614.841.41.002.71

[Abstract] An analysis and examination of a railroad accident in Alma-Ata in 1989 involving a collision and rupture of a tank car containing liquified propane and butane and a subsequent explosion with formation of a "fire ball" were presented. It was assumed this accident would be typical of such accidents which might occur at chemical enterprises. The analysis confirmed the correctness of existing ideas concerning the course of accidents with formation of "fire balls". Compilation of sound operational plans for eliminating such accidents requires consideration of the findings of this analysis according to the dynamics of increase of pressure in a tank containing liquified hydrocarbon gases, engulfed in flame. The work of emergency services in the fire zone, during such an accident, should cease at the moment of filling of the tank by the liquid phase, when its rupture is likely at any moment. Relationships developed in the analysis made it possible to assess the time of filling of the tank by the liquid phase in each specific case and the cooling effect of water applied may be calculated. Safety precautions included cessation of all rescue operations firefighting and cooling of the tank and withdrawal of all persons to a safe distance to prevent injury when formation of a "fire ball" appears to be imminent. Figures 2; references 8: 4 Russian; 4 Western.

Production of Ammonium Polyphosphates Based on Ammonization of Impissated Extraction Phosphoric Acid in Tubular Reactor

[Article by V. N. Kochetkov and Ye. V. Tulina]

UDC 661.635.213.002.237

[Abstract] Experiments performed on a model type device were used to determine optimum conditions of ammonization of extraction phosphoric acid with addition of carbamide and development of an efficient design of a tubular reactor in order to produce a melt of ammonium polyphosphates with the highest possible level of condensed forms of P_2O_5 and the most complete use of ammonia and heat of the chemical reactions. The feed of additional heat into the tubular reactor ensured production of a melt of ammonium polyphosphates with a high degree of conversion of P_2O_5 and decrease of the gradient of temperatures between the outer and inner walls of the reactor which then decreased encrustation of the inside of the reactor. The additional feed of heat, with the quantity regulated by a change of voltage from 30 to 100 V greatly affected formation of condensed forms of P_2O_5. The rate of formation of condensed forms of P_2O_5 increased with the increase of voltage in the electric circuit and the molar ratio $NH_3:P_2O_5$ equal to 5. Figures 6; references 3 (Russian).

Stress State of Drill Pipe Frame Elevator

[Article by E. E. Abdulaliyev and A. N. Salin, Candidates of Technical Sciences]

UDC 539.319.001.5:622.24.057.2

[Abstract] A study is made of the stress state of a 2500 kN drill string elevator by a polarization optical method using frozen three-dimensional models made of a polymer material. The epoxy model was made in 1:3 scale, force scale 1:14,700. Curves showing the stresses acting on the main cross sections of the body of the pipe elevator are presented. The maximum stresses in the cylindrical portion do not exceed the yield point of the material of the elevator. There is an area in the upper portion of the elevator body in which the stresses are slight, indicating the possibility of decreasing the dimensions of the structure in this area. This would allow a five percent decrease in the mass of the elevator. The stress level in the lugs could be reduced by increasing the radius of the toroidal surface of each lug. The metal consumption of the gate could also be reduced. Figures 3; Reference: 1 Russian.

Calculation and Experimental Estimate of Influence of Local Dents on Strength of Vessels and Equipment

[Article by V. N. Mukhin, Candidate of Technical Sciences, and V. I. Elmanovich]

UDC 539.319.004.17:665.5.002. 5

[Abstract] The scientific research institute of chemical machinery has developed RD 26-6-87, the first standards document calling for consideration of deviations from ideal circular shape in calculating the strength of cylindrical shells. The calculation methods in this document allow the permissible internal pressure in the body of a vessel or of chemical equipment with a dent to be calculated. This article presents a comparison of the results of such calculation estimation of the strength of bodies with dents with tensometric data, comparing the maximum stress in the wall of a body at the point where the dent is located with the calculated stress. The tensometry demonstrated that a local dent acts as a stress concentrator, with the greatest stress at the center of the dent and with greater circular than axial stresses. There is a zone around the edges of a dent where the stress is lower than the nominal value for the entire structure. Permissible dent dimensions in vessels and equipment should be determined not on the basis of strength or permissible stresses, but rather on the basis of deformation failure criteria. Equations are presented for this purpose. The criterion developed was used to determine the possibility of using dented vessels. It is noted that when a dent is formed, microscopic cracks may also be formed, which must be considered in determining the need to repair a vessel. Figures 3; References: 12 Russian.

Thermal Reliability of Bimetallic Ribbed Pipe in Air Cooling Equipment

[Article by V. B. Kuntysh, Candidate of Technical Sciences]

UDC 621.593-462-408.8

[Abstract] The purpose of this article is to establish a reliable value of the permissible air temperature at the inlet to air cooling equipment consisting of pipes with both commonly used types of ribs, assuring stable thermal characteristics of the equipment. The problem was solved by a calculation and analytic method utilizing equations derived in the study for the heat transfer and aerodynamic resistance of ribs of the types studied to calculate the heat flux and required fan drive power for a specific design of air cooling equipment and fan operating mode. Thermal calculations were performed assuming ideal contact between tubes and ribs and at the actual values of thermal resistance corresponding to the calculated temperature conditions. Selection of air cooling equipment considering the maximum permissible air temperature for a specific type of ribs is said to guarantee that the equipment will provide the desired heat flux under its standard usage conditions. Figures 3; References: 5 Russian.

Separation of Isotopes of Helium by Low-Temperature Fractional Distillation

927M0018C Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 6, June 1991 pp 28-30

[Article by A. S. Bronshteyn and I. F. Kuzmenko, Candidates of Technical Sciences]

UDC 66.048

[Abstract] Previous theoretical analyses of the number of theoretical contact stages required for separation of He^3 and He^4 cannot be considered satisfactory, since they do not give the relationship between the thermal mode on the condensor and the number of theoretical contact stages. This article presents a calculation in which the quantity of gas G and liquid L is adjusted for each stage based on the changing heat of evaporation of the mixture and the local relative volatility of each component. In the course of the numerical study an analysis was also performed of the influence of concentration and vapor content at the input of the mixture into the column. The algorithm and a program for thermodynamic calculation of fractional distillation of helium mixtures can establish the preliminary regularities and characteristics of the process and serve as a basis for solution of a multiple-parameter optimization problem for a separation unit in combination with a refrigeration system. Figures 4; References 8: 2 Russian, 6 Western.

Determination of Air Penetration Time in Gas Discharge Tubes

927M0018D Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 6, June 1991 pp 30-31

[Article by Yu. A. Khristenko, Yu. A. Kondrashkov, Candidate of Physical- Mathematical Sciences, and V. P. Tomilin, Candidate of Technical Sciences]

UDC 614.833.4

[Abstract] When a gas discharge tube is left filled with hydrogen, air, a heavier gas, begins to displace the hydrogen, forming a potentially explosive mixture. Studies to determine the time required for penetration of air into such a vertical tube were performed on two tubes 4 m in length and 0.052 and 0.2 m in diameter. A horizontal tube was also tested, as well as tubes with exhaust points at the top and bottom. Equations are produced to calculate the filling times for these tubes. Figures 2; References: 2 Russian.

Production of Absorptive Coating on Copper

927M0018E Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 6, June 1991 pp 31-32

[Article by L. M. Ebel]

UDC 669.3-761

[Abstract] The purpose of this work was to select coatings for use in cryogenic equipment with a radiation coefficient of about 0.9, to develop a technology for application of the coatings and to check the possibility of using these coatings at temperatures near liquid nitrogen temperature. Methods of producing coatings tested included electrochemical oxidation, production of black nickel, black chromium and application of dielectric layers of organic origin. Coating technologies were studied on copper plates measuring 50 x 50 mm with initial roughness Ra = 0.32-0.63. The highest coefficient of radiation was that of K-300-61 glue consisting of a mixture of two resins. The work established that the most suitable coating consists of several layers of organic substances. Figures 2; References: 3 Russian.

Elimination of Internal Defects in Aluminum Equipment Castings

927M0018F Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 6, June 1991 pp 34

[Article by I. A. Maksunov, B. I. Velishek]

UDC 621.747.59:621.646-034.71

[Abstract] The "Lenpromarmatura" scientific-production association has studied the possibility of producing high-quality castings of aluminum alloys by hot isostatic pressing. The essence of the method is as follows: a defective casting is placed in a special sealed cylindrical chamber. An inert gas such as argon or helium is pumped into the chamber until an assigned pressure and temperature are reached. The casting is held under these conditions for a certain time. The cycle is repeated if necessary until the casting defects are healed. This treatment was found to double or triple the tensile strength and increase hardness by 23 to 40 percent. X-ray studies showed that internal defects were reduced in volume by 5-10 times and disappeared completely at 500°C. The method selected for future use is: temperature 500°C, pressure 150 MPa, time 3 hours.

Manufacture of Welded Products of High-Molecular Mass Low-Pressure Polyethylene

927M0018G Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 6, June 1991 pp 36

[Article by M. I. Yershov, E. N. Vilenskiy, V. A. Safonov and T. A. Puganova]

UDC 678.5.09.43:678.742.21

[Abstract] Products of high-molecular-mass low-pressure polyethylene (HMMLPP) with mean molecular mass 1 million or higher are unsuitable for gluing. This requires the development of welding methods. Studies performed

indicates that the optimal method involves insertion of a heating tool between the two pieces to be welded together, application of a force of up to 1.5 MPa, heating of the tool with a current density of $20.2 \cdot 10^{-6}$ A/m^2 for 80 s, releasing the pressure and withdrawing the heating tool, increasing the pressure to 2.3 MPa, holding for 120 s, reducing the pressure and removal of the part. The entire welding cycle lasts 200 s. The tensile strength of the welded seam thus produced is 15.8-26 MPa, 96-98% of the tensile strength of the material. However, the HMMLPP loses some of its plasticity in the area of the welded joint. Preliminary calculations indicate that development and introduction of an installation for welding of cathode cell frames at Norilsk metallurgical combine would have an annual economic effect of at least 130,000 rubles. The use of this welding process could greatly expand the use of HMMLPP in various industries for the manufacture of products to be used in corrosive media and friction couples. References: 2 Russian.

Chain Thermal Explosions

[Article by V.V. Azatyan and A.G. Merzhanov, Structural Macrokinetics Institute, USSR Academy of Sciences, Chernogolovka]

UDC 541.11;126

[Abstract] The authors of the study reported herein conducted a theoretical and experimental investigation of thermal explosions in different types of reaction systems based on the branched-chain reaction mechanism. They begin by examining the main factors responsible for the differences between thermal explosions in systems reacting by means of simple mechanisms (unilateral zero- and first-order reactions and simple self-catalysis by the end product) and thermal explosions involving branched-chain reactions. They determined that because of the law of the "double exponent" of the temperature dependence of the rate at which a branching chain combustion reaction develops, a reaction becomes a thermal explosion not only in the case of intensive energy release but also when the activation energies of the limiting stage of the process are very low. They confirm this fact by presenting data from a series of four experiments examining the thermal explosion of H_2 with O_2 that was conducted on a static vacuum unit at different initial pressures. Specifically, they find that despite the relatively low branching stage activation energy of the combustion of H_2 mixed with O_2 (i.e., 16.6 kJ/mol), the resultant thermal explosion is very sharp, and the conditions of the transition from chain combustion to a chain thermal explosion manifest a distinct criticality. This is explained by the fact that as had been shown earlier, under conditions in which the branching of chains predominates over quick release, the increase in the rate of a branched-chain process with temperature is a much stronger one corresponding to Arrhenius' law. The authors also determined the range of initial pressures, temperatures, and reaction mixture compositions resulting in a branched-chain explosion. The data indicated that close to the first explosive range in the absence of trimolecular reactions, chain combustion occurs without any noticeable spontaneous heating. This was true even at a threshold of 6-7 torr (the diffusion range of the breaking of the chains). Preexplosion heating and the homogeneous self-inhibition of branched-chain processes are also examined. The participation of elementary reactions of different kinetic orders in competition with the branching and breaking of the reaction chains are deemed responsible for the specific nature of the dependence of the laws of chain combustion as a function of the pressure of the reaction mixture. In the concluding stage of their analysis, the authors focus on thermal explosion in the vicinity of the first explosive range. They conclude that heterogeneous breaking of the chains plays virtually no role and that heat release through the reactor walls is the only channel of energy release from the reaction medium. The thermal explosion of a mixture of H_2 with O_2 is compared with chain thermal explosions occurring in other compounds (SiH_r, GeH_4, and SiH_2Cl_2). Figures 5; references 35: 29 Russian, 6 Western.

Asymptotic Behavior of a Stationary Nonadiabatic Combustion Wave

[Article by S.I. Khudyayev, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Chernogolovka]

UDC 536.46:532.5

[Abstract] In a continuation of the effort to develop an asymptotic theory of combustion, the author of this article considers the main term of the asymptotics of a combustion wave in the presence of heat losses. This same topic has been formulated and addressed by a number of other researchers. The difference between the models proposed by those individuals and the one proposed here is that the author of the present article rejects those researchers' a priori assumption of incomplete transformation in the combustion zone. He cites yet another work demonstrating that the aforesaid assumption is not always valid. In the first half of this article, the author devotes his attention to the asymptotics of the combustion wave of a very simple condensed system. In the second half, he turns his attention to the asymptotics of the combustion wave of very simple gaseous mixtures. A total of 62 equations or sets of equations are presented. His equation model of the asymptotics of the combustion wave of gaseous mixtures is similar to those equations presented for a condensed system. The equation system for the gaseous mixtures contain a diffusion term, however. The results presented in this article are said to apply to that parameter range in which complete transformation in the combustion zone does take place. The author does, however, discuss the differences between the cases where the Lewis number equals 0 and where it does not. References 20: 17 Russian, 3 Western.

Calculating Explosive Processes in Condensed Explosives

[Article by S.A. Gubin, V.V. Odintsov, and V.I. Pepekin, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Moscow]

UDC 534.222.2+536.7

[Abstract] This review begins with a brief description of the two common methods of making thermodynamic calculations of explosive processes (including detonation), i.e., the equilibrium constants method and the

method of the extremum of characteristic functions. Progress in thermodynamic calculations in the area of detonation and explosion is reviewed. Particular emphasis is placed on the following topics: the formation of a diamond phase of carbon in the products of the detonation and explosion of high-power individual and mixed graphite-free explosives, the presence of a transition leg of the dependence of detonation parameters on the initial density of the explosive and on the detonation rate on account of a replacement of the phase state of the carbon in the detonation products, and the effect of the dispersion of solid carbon on the parameters of graphite-diamond equilibrium and on the position of the transition leg. Progress in the research on the behavior of a detonation product behind a detonation wave and during the process of isentropic discharge and in the development of a thermodynamic model specifying the propellant capability of explosives is also discussed. The authors conclude by stating that thermodynamic calculations and modeling of explosive processes (1) make it possible to research process details that could not otherwise be studied and (2) have practical applications in the making of engineering estimates and design decisions. Figures 5, table 1; references 24: 20 Russian, 4 Western.

Three-Stage Model of Fuel Combustion During Luminous Irradiation

[Article by N.S. Zakharov and S.A. Kazarin]

UDC 536.46

[Abstract] The authors of this concise report consider a three-stage model of combustion under the effect of optical radiation with a flux density up to 10 kW/cm^2. Their model gives consideration to the absorption of radiation energy in the starting substance and in the reaction products. They formulate and solve five equations by using familiar finite differences methods based on implicit numerical schemes by decomposing the exponents into the rates of heat release base on Frank-Kamenetskiy's method and by using iterations to determine the heat release function. They succeed in deriving spatiotemporal temperature and concentration dependences and establish the effect of radiation flux density on combustion rate. According to their calculations, for initial flux densities up to the aforesaid value of 10 kW/cm^2, the combustion rate is linearly dependent on luminous flux density. This finding is in good agreement with experimental data reported elsewhere. Figures 3; references 12 (Russian).

The Effect of the Initial Parameters of a Fuel Mixture on the Toxicity of Exhaust Gases From an Internal Combustion Engine

[Article by M.M. Rusakov, A.P. Shaykin, and V.V. Karpusenko, Tolyatti Polytechnic Institute]

UDC 621.434

[Abstract] Because of the increasing urgency of reducing the amount of toxic emissions from internal combustion engines, the authors of this concise report examined the effect of initial fuel mixture parameters on the toxicity of exhaust gases from internal combustion engines with spark-plug ignition. They examined the temperature parameters and toxicity of exhaust gases for different fuel-and-air mixtures and different temperatures at the end of the intake. The studies performed showed clearly that the content of toxic substances in exhaust gases is indeed a function of the initial parameters of the fuel-and-air mixture and their minimal concentration range. The minimal exhaust gas toxicity (given a degree of compression between 8 and 12) is reached when the excess-air coefficient (α) is between 1.8 and 2.0 and the temperature at the intake is between 300 and 400°C. The authors conclude that preliminary burning (oxidation) of part of the fuel-and-air mixture at the intake is the most promising heating method. Figure 1; references 8: 6 Russian, 2 Western.

The Phase Diagram of the System Cu-Mn-O

[Article by Yu.V. Golikov, L.A. Ovchinnikova, R.G. Zakharov, V.P. Barkhatov, I.N. Dubrovina, and V.F. Balakirev, Metallurgy Institute, Ural Department, USSR Academy of Sciences, Sverdlovsk]

UDC 541.123:546.56:711'21

[Abstract] The authors of the study reported herein constructed an equilibrium phase diagram of the system Cu-Mn-O in air based on in situ high-temperature x-ray studies. For their studies they synthesized (according to the ceramic method) solid solutions and heterogeneous composites with the general formula $Cu_xMn_{3-x}O_m$ ($0 \leq x \leq 1.60$; $\Delta x = 0.05$). The increment of Δx selected was the minimal possible to be able to use the given method and was half the amount used previously by Drissens and Rieck. A DRON-3.0 diffractometer was used for the high-temperature x-ray analysis (with CuK_α radiation, a monochromator made of pyrolytic graphite, and a UVD-2000 high-temperature attachment). Specimens were produced by annealing in air at temperatures of 700, 750, 800, 850, 870, 880, 900, 920, 950, 1,000, 1,060, 1,100, 1,150, 1,200, 1,250, 1,300, 1,350, and 1,400 +/- 10°C for 96 to 1,250 hours depending on the synthesis temperature. The resultant data were plotted in a phase diagram of the system Cu-Mn-O in air. The study data led the authors to conclude that the phase equilibria temperatures of α-Mn_2O_3-βMn_3O_4 = 883.6°C and β-Mn_3O_4-γ-Mn_3O_4 = 1,172°C that have been published by others are indeed the most precise. The authors compare their own findings to those of Drissens and Rieck as published in 1967. The most noticeable discrepancies were observed at temperatures above 1,150°C. The authors of the present study find a much narrower region of the homogeneity of solid solutions with a spinel structure. An entire series of compositions that the previous authors deemed homogeneous were found to be two-phase compositions in the present study. The differences between the phase diagrams constructed by the two groups of researchers are discussed in detail. Figures 2; references 13: 5 Russian, 8 Western.

Metastable States in Systems Consisting of Hydrogen and an Intermetallic Compound

[Article by V.Z. Mordkovich, State Scientific Research and Design Institute of the Nitrogen Industry and Organic Synthesis Products, Moscow]

UDC 546.3-19'11

[Abstract] The author of the study reported herein studied the desorption isotherms in systems of the type $Ce_xLa_{1-x}Ni_{5-y}Al_y$-H_2 (where x = 0 to 0.8; y = 0 to 0.6). Specifically, they determined the desorption isotherms of the hydrides $LaNi_5$, $Ce_{0.5}La_{0.5}Ni_5$, and $Ce_{0.7}La_{0.3}Ni_5$ at room temperature at at 373 K. For each of the intermetallic compounds studied, the plateau on the desorption isotherm was found to be shorter at 373 K than at 293 K, or else it was found to be absent altogether at 373 K. When the content of cerium in the solid solution $Ce_xLa_{1-x}Ni_5$ is increased, the shortening of the isotherm as the temperature increases became more rapid. In other words, the critical temperature was reduced. For $Ce_{0.7}La_{0.3}Ni_5$, in particular, the critical temperature was 360 +/- 10 K as opposed to a critical temperature of about 480 K for $LaNi_5$. Instead of using the conventional hydrogen saturation technique (which calls for initially heating the specimen in a vacuum from T_0 to T_1 and then saturating the intermetallic compound with hydrogen at T_1 while raising the pressure to P_1) the authors used an alternative hydrogen saturation method. According to this alternative method, the specimen was saturated with hydrogen at T_0 and then heated to T_1) at a constant pressure. When the alternative hydrogen saturation technique was used in the case of $Ce_{0.7}La_{0.3}Ni_5$, severalfold more hydrogen was dissolved in the specimen than is the case in classical experiments. Accordingly, the desorption isotherm obtained after such saturation was found to look entirely different. It did not, however, depend on the maximum saturation pressure, which was varied from 4 to 35 MPa in the individual experiments. The authors also plotted a three-dimensional pressure-temperature-hydrogen concentration diagram for the system intermetallic compound-hydrogen with a metastable phase. The diagram demonstrates that at temperatures above 373 K the "metastable" and "equilibrium" surfaces begin to approach one another. They coincide at 423 K. In their analysis of the reasons limiting the series of intermetallic compounds for which a metastable state may be observed to the conditions x > 0.5 and y < 0.1, the authors note the connection between these conditions and the critical temperature in the system H_2-intermetallic compound. They note that the critical temperature in the system H_2-$LaNi_5$, for example, is 480 K, which is much higher than the threshold temperature of the existence of a metastable phase. Figures 2; references 15: 5 Russian, 10 Western.

Kinetic Aspects of Selected Deep Oxidation Reactions for Environmental Protection

[Article by S.L. Kiperman, Organic Chemistry Institute imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow]

UDC 541.128.13

[Abstract] Working jointly with researchers from the Dzerzhinsk affiliate of the State Scientific Research

Institute of Industrial and Sanitary Gas Scrubbing [NIIOGAZ], the authors of the present study examined the kinetics of selected deep oxidation reactions of various classes of spherical compounds on platinum catalysts. The studies encompassed a wide range of organic compounds, including saturated hydrocarbons, aromatic hydrocarbons, alcohols, aromatic alcohols, aldehydes, esters, carbon oxide, and mixtures of the aforesaid compounds. The compounds were studied in concentrations in air ranging from 0.2 to 80 x 10^{-4} mol/m^3 and at temperatures ranging from 100 to 400°C. Aluminum-platinum catalysts (primarily AP-54 and AP-64) were used. The deep oxidation reactions were performed under steady-state conditions and were then extended to non-steady-state (transient) conditions. A close-to-100% selectivity was achieved in most cases, and the reaction products generally turned out to be carbonic acid and water (in the case of nitrogen-containing compounds, up to 5% nitrogen oxides also resulted along with molecular nitrogen). The following are among the main conclusions of the studies performed. Because the kinetic models of reactions of the deep oxidation of small amounts of organic compounds are very diverse, any attempt to describe all such reactions in terms of first-order equations must be deemed unacceptable. Studies of the transient processes occurring in deep oxidation reactions confirms that the said reactions differ greatly from such standpoints as the nature of the reaction of the individual components, the predominant participation of certain surface centers, and the nature and strength and also the reactivity of the resultant intermediate adsorption bonds of the starting components. The courses of deep oxidation reactions of the study compounds may be controlled by varying the reaction conditions. Specifically, this was evident in the predominant role of gaseous oxygen at low temperatures as the role of the mobile portion of the surface oxidation increases at high temperatures. The role and ratio of the reactivity of the reduced and oxidized segments of the surface of platinum catalysts were also found to be highly temperature dependent. Kinetic models of the deep oxidation of mixtures of given organic compounds may, in a number of cases, be predicted successfully by proceeding from the principle of a simple mutual effect and by using data on the kinetics of the individual reactions involved. The validity of this approach was confirmed by experiments conducted at the Dzerzhinsk affiliate of the NIIOGAZ. The study data reported here were used to design and construct catalytic purification reactors that were then used to clean groups of very difficult to clean substances. A system of 16 components resulting from the production of synthetic fatty acids was, for example, broken down into five groups containing the following difficult-to-oxidize components: acetic acid, acetaldehyde, propanol, ethyl acetate, and carbon oxide. The results confirmed (1) the validity of the principle of simple mutual effect and (2) the feasibility of using the newly established kinetic models as a basis for designing effective commercial catalytic purification processes. Figures 7; references 33: 28 Russian, 5 Western.

Optimal Dispersivity of Heterogeneous Catalysts

[Article by G.I. Golodets, Physical Chemistry Institute imeni L.V. Pisarzhevskiy, UkSSR Academy of Sciences, Kiev]

UDC 541.128.13

[Abstract] The dispersivity (average crystal size, i.e., d) of the active component of a catalyst may have a significant effect on a number of critical catalyst characteristics. A catalyst's dispersivity affects its concentration of complex active centers (the preexponential factor of the rate constant of the limiting stage). Specifically, increases in d result in increased reaction rates. Dispersivity has also been shown to affect the adsorption heat of the dominant intermediate compound: the adsorption heat increases as the crystal particle size increases until heat saturation is reached (when d is approximately 10 to 20 nm). A catalyst's productivity is also affected by its dispersivity: A catalyst's specific surface is inversely proportional to the square of its average particle size. Thus, while increased values of d are associated with increased concentrations of complex active centers and higher adsorption heats, they also result in a decrease in specific catalyst surface. This conflict gives rise to the concept of an optimal catalyst dispersivity. Under certain conditions, d_{opt} may be the consequence of just one factor (i.e., adsorption heat). This is especially true in the case of hydrogenation reactions of the second type that include the intermediate formation of adsorption complexes that are highly bound to the surface (such as hydrogenation of CO and the synthesis of ammonia on metal catalysts). Optimal values of d determined by varying just the adsorption heat will not coincide with values of d_{opt} determined by proceeding from the competition of the changes resulting from varying the concentration of active centers, heat of adsorption of the dominant intermediate compound, and the catalyst's specific surface area. The value of d has also recently been demonstrated to affect the manifestation of a "strong metal-carrier interaction" effect. This effect has been shown to be maximum in the case of situations wherein the particle size of the metal is close to the pore size of the carrier. Because selectivity (like activity) is a primarily a function of the energy of the intermediate chemical reaction of reagents and catalyst, a catalyst's dispersivity also affects its selectivity. Figures 2; references 16: 13 Russian, 3 Western.

The Role of the Carrier in the Formation of the Active Phase of Catalysts of the Hydrogenation of Carbon Monoxide

[Article by G.K. Kamalov, Ye.Yu. Povolotskiy, O.A. Silantyeva, and Chey En Man, Physical Chemistry Institute imeni A.V. Bogatskiy, UkSSR Academy of Sciences, Odessa]

UDC 541.128.3:542.941.7:546.262.3-31

[Abstract] Most research on the role of the carrier in the formation of the active phase of catalysts of the hydrogenation of carbon monoxide has focused on individual oxides or else on mixtures of oxides with a complex phase profile. This has resulted in discrete uncontrollable changes in many carrier parameters and has made it impossible to explain the effect of a carrier's individual characteristics on the properties of the resultant contacts. In an effort to remedy this methodological problem, the authors of the study reported herein decided to conduct their studies on model carriers representing solid solutions of metal oxides that are capable of maintaining the structural and electrophysical characteristics of their matrices virtually without change given a low content of modifier. Specifically, they studied the effect that the donor-acceptor properties of the surface of 5% solutions of metal oxides in an aluminum oxide matrix have on the activity of nickel- and cobalt-containing catalysts of the hydrogenation (methanation) of carbon monoxide. Three methods were used to test the donor-acceptor properties of the surface of the binary oxides studied: the pH of an aqueous suspension of the specimens, the value of Δv_{CO} in the IR spectra of the adsorbed carbon monoxide, and the adsorption heats of ethane and ethylene. The catalytic activity of the resultant contacts was measured in a continuous unit at 523 K at atmospheric pressure. X-ray phase analysis indicated that all of the carriers synthesized were characterized by a low degree of crystallinity. They may be classified as γ, η, or δ forms of Al_2O_3, and none was found to exhibit reflexes corresponding to injected oxide phases. Only Al-Cr, Al-Mn, and Al-Fe solid solutions were found to possess a noticeable ability to absorb hydrogen at temperatures below 723 K. The studies performed led the authors to hypothesize that the donor-acceptor properties of the carriers' surface affect the charge state (degree of reducibility) of the metal-catalyst and ultimately determine their activity in the series of 2% solutions studied. The donor-acceptor properties of the different carriers studied were found to exert different effects on the catalytic properties of the active phase depending on its degree of reducibility. This finding in turn led the authors to hypothesize a noticeable difference in the mechanisms of the hydrogenation of carbon monoxide on contacts characterized by different metal-catalyst charge states. The systems studied were recommended for use as a convenient model during research on the laws governing the formation of the active phase of catalysts of the hydrogenation of carbon monoxide. Figures 7, table 1; references 20: 19 Russian, 1 Western.

The Mechanism of the Reaction of NO With CO on Oxide Catalysts

[Article by T.G. Alkhazov and G.Z. Gasan-zade, Azerbaijan Petrochemistry Institute (AzINEFTEKhIM), Baku]

UDC 541.128.13

[Abstract] The authors of the study reported herein examined the mechanism of the reaction of nitrogen monoxide and carbon monoxide on group IV transition metal oxides and composites based on them. The reactions were performed in pulse and continuous nonchromatographic modes with a vibration-rarefied catalyst layer as described elsewhere. The gas mixtures were subjected to chromatographic analysis to determine their contents of O_2, N_2, NO, N_2O, CO, and CO_2. High-purity helium was used as the diluent gas. The generally accepted methods were used to measure the catalysis rates on the different catalyst specimens and the individual reaction rates of the reagents given different degrees of surface reduction (θ). The rates of catalysis on the different catalyst specimens were found to exceed the reaction rates of the individual reagents with the catalyst. During their research, the authors also encountered instances where the equality of the individually measured reduction and oxidation reaction rates of NO and CO with a catalyst was achieved at values of θ that differed significantly from the degrees of surface reduction corresponding to a steady-state catalyst (θ_{steady}). As θ increased, the rate at which CO reacted with a chromium oxide catalyst diminished continually. The reaction rate of NO with the catalyst increased as θ increased. Identical reduction and oxidation rates were achieved when θ equaled or approximated 0.4. The catalytic reaction rate was also found to increase as θ increases. The degree of surface reduction corresponding to θ_{steady} = 1 was found to differ from that degree of reduction at which the equality of the individually measured reduction and oxidation rates is reached. Unlike in the case of many oxide catalysts, in the case of NiO, the authors found that the rate of both reduction and oxidation reactions increases as θ increases. Equality of the oxidation and reduction reaction rates is achieved when θ equals or approximates 0. The rate of catalytic reaction on this same catalyst also increases as θ increases. The catalyst reaches a steady state at the very same values of θ_{steady} as when equality of the reaction rates of the individual reagents with the catalyst rates is reached. Even in this case, however, the catalysis rate turns out to be much higher than in the case of reduction and oxidation reactions. The authors explained these findings based on the principles that (1) a catalyst's steady state is determined not only by its own chemical makeup but also by those substances that are on its surface in an adsorbed state and (2) the rate of a reduction reaction with a catalyst that has first been brought to a steady state consists of the rate of the reduction of the catalyst itself and the rate of its interaction with the adsorbed fragments that are on its surface. The authors conclude that the study reaction occurs in accordance with a fused (unified) mechanism that includes a stage of nitrosyl complex formation. The authors further conclude that catalysts selected for the study reaction should contain complexing elements (Fe, Co, Ni, and others) capable of

forming diverse series of complex compounds. Rhodium, ruthenium, and palladium are recommended for this purpose. Figures 3, tables 3; references 21: 15 Russian, 6 Western.

Deep Oxidation of Hydrocarbons and Gasoline Effluents on Applied Oxide Catalysts

[Article by V.A. Zazhigalov, V.M. Belousov, G.A. Komashko, and A.I. Pyatnitskaya, Physical Chemistry Institute imeni L.V. Pisarzhevskiy, UkSSR Academy of Sciences]

UDC 541.128.1+547.214

[Abstract] In a continuation of research to improved the techniques available for deep oxidation of hydrocarbons and gasoline effluents on applied oxide catalysts, the authors of the study reported herein compared the use of two techniques for applying the active mass onto the carrier. Specifically, they compared the techniques of impregnating the carrier by element salts and securing the elements on the surface by the formation of a chemical bond with the carrier's functional groups (i.e., grafting). VO_x and Co-Cr-O catalysts were studied along with the following carriers: aerosil-200; four types of TiO_2 (anatase, rutile, 35% rutile + 65% anatase, and TiO_2 obtained from $Ti(i\text{-}OC_4H_9)_4$); aerosil-200 with a monolayer of Ti attached to the surface; silica wafer; SiC, activated charcoal; carbon fabric; and Al_2O_3. The carriers were impregnated with aqueous solutions by using $NH_4VP_3 + C_2H_2O_4$ or nitric acid salts of Co and Cr. The elements were grafted in CCl_4 by using $VOCl_3$, $CoCl_2$, and CrO_2Cl_2. All of the specimens were heated to 873 K in air with the exception of the activated charcoal and carbon fabric, which were heated to 673 K in a vacuum. The catalytic properties of all of the specimens were studied on a continuous-type unit. Regardless of the individual type of carrier used, the catalysts prepared by impregnation were less effective in processes of oxidizing paraffin hydrocarbons than were catalysts produced by the grafting technique. Of all the grafted specimens, those with the SiO_2 carriers were least effective, whereas those with TiO_2 carriers were most promising. The best of the contacts, i.e., V/TiO_2, were tested in reactions of the oxidation of gasoline effluents and proved to be quite effective. The studies performed led the authors to conclude that the grafting technique best increases the active component's dispersivity and thus results in the most effective catalysts for deep oxidation of hydrocarbons (paraffins) and gasoline effluents with a significant reduction in the amount of applied active component used and with a low temperature of catalytic reaction onset. Figures 3, tables 3; references 11: 6 Russian, 5 Western.

Mechanism of the Conduction of Thin Composite Polyethylene-Metal Films

[Article by M.A. Manoylo, B.G. Mischanuk, and E.N. Korol, Physical Chemistry Institute imeni L.V. Pisarzhevskiy, UkSSR Academy of Sciences]

UDC 539.23+541.67

[Abstract] The authors of the study reported herein examined the mechanism of the conduction of thin polyethylene-metal (Ag, Cu, Al) composite films. The study films were produced by the method of thermal vacuum deposition of high-pressure polyethylene (All-Union State Standard [GOST] 16337-70) and metal on a VUP-5 commercial universal vacuum unit. Nonconductive plates that had been presprayed with silver stripes to create ohmic contacts with the films to be sprayed were used as bases. This procedure resulted in a surface-type cell that was then used to determine the conduction σ of the sprayed film. The ellipsometric method was used to measure the films' thickness, and the sign of the charge carriers in the film was determined based on the sign of the thermoelectromotive force. A copper-constantan thermocouple sprayed onto the film surface was used to measure the film temperature when the temperature dependences of σ were determined. The authors studied composite Ag + polyethylene, Al + polyethylene, and Cu + polyethylene films 10^{-5} cm thick with n-type conduction and with σ (at 300 K) values of 2 and 6 x 10^{-5} $\Omega^{-1}cm^{-1}$ in the case of polyethylene + Ag, 7 x 10^2 $\Omega^{-1}cm^{-1}$ for Al + polyethylene, and 4 x 10^2 $\Omega^{-1}cm^{-1}$ for Cu + polyethylene. The conduction of the polyethylene + Cu and the polyethylene + Al films was determined to be based on the tunnel mechanism regardless of temperature. The polyethylene + Ag films also manifested tunnel-type conduction at low temperatures. At temperatures above 333 K, however, the conduction of the polyethylene + Ag films appeared to be conditioned by the conduction of the polymer matrix. The authors further stated that conduction at temperatures above 333 K was also likely to occur in accordance with other mechanisms as well; the nature of these mechanisms was left as a subject for future research studies, however. Figures 2; references 6 (Russian).

The Chemical Gaseous-Phase Precipitation of Boron Carbide From a BCl_3-C_7H_8-H_2 Mixture Onto a Heated Substrate

[Article by Yu.M. Grigoryev, V.A. Shugayev, A.S. Mukasyan, N.G. Samoylenko, and A.A. Shiryayev, Structural Microkinetics Institute, USSR Academy of Sciences]

UDC 661.665.3

[Abstract] The authors of the study reported herein examined the gaseous-phase precipitation of B_4C from a BCl_3-C_7H_8-H_2 mixture onto a heated tungsten filament in a noncontinuous reactor. The B_4C was deposited onto an electric current-heated tungsten filament 75 μm in diameter and 70 mm long. The electrothermograph used in the experiment made it possible to achieve temperatures between 1,300 and 1,700 in 40 ms and to maintain them during the entire course of the experiment by means of brightness signal feedback. Lengthwise and crosswise polished specimens were produced from the coated filaments and analyzed on an ICXA-733 Superprobe x-ray microanalyzer. The specimens were also subjected to analysis by a DRON-2 diffractometer, and the microhardness of the films was measured by a PMT-3. Using a noncontinuous reactor made it possible to specify the composition of the starting mixture given any component ratio. The equilibrium composition of the reaction products was characterized in terms of the parameters η and Z, which represent the ratio of the partial hydrogen pressures and boron chloride (η = P_{H2}/P_{BCl3}) and boron chloride and toluene (Z = P_{Cl3}/P_{C7H8}). Boron carbide with a close-to-stoichiometric composition was obtained when Z was between 20 and 30. According to calculations based on the composition of carbon in the condensate that were made for these very conditions, the content of carbon in the precipitate decreases as Z increases. The experimental curve plotted is more strongly dependent on the value of Z, however. The calculated and experimental curves for a temperature of 1,600 K are closer to one another than is the case for a temperature of 1,450 K. An examination of the effect of synthesis temperature on the film's density, microhardness, and carbon content revealed that as the synthesis temperature rises, the carbon content increases somewhat when compared with the case of a stoichiometric boron carbide composition. As the temperature increases, the film's density decreases from 2.5 to 2.35 g/cm³ (which is evidently related to the film's increased carbon content). The microhardness of the boron carbon was found to change little as the synthesis temperature increased and was found to equal 5,000 +/- 200 kg/mm² with an indenter load of 200 g. An examination of the effect of the parameter Z on the makeup of the condensed products formed in the deposition process revealed the presence of β-WB, WC, and W phases in addition to B_4C and carbon. The amount of B_4C and pyrolytic graphite present was determined to be significantly dependent on the BCl_3:C_7H_8 ratio. An increase in Z led to a reduction in the content of pyrolytic graphite in the precipitate. The experimental data were in agreement with the thermodynamic computation results and confirmed the complex nature of the parametric dependence of the makeup of precipitation products in the system BCl_3-C_7H_8-H_2. The experiment results may thus be used in developing ways of controlling the said precipitation process. Figures 4; references 9: 4 Russian, 5 Western.

The Heat Stability of Intercalation Compounds of Fluorinated Graphite With Organic Solvents

[Article by V.G. Makotchenko, A.S. Nazarov, G.S. Yuryev, and I.I. Yakovlev, Inorganic Chemistry Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk]

UDC 546.26-162

[Abstract] The authors of the study reported herein examined the x-ray phase and chemical changes occurring when intercalation compounds of fluorinated graphites are heated. Specifically, they studied compounds of the composition $C_xFCl_y \cdot zR$, where x ≃ 2.13 to 2.21, y ≃ 0.07 to 0.1, and R = methanol, n-propanol, n-octanol, pentane, heptane, acetone, benzene, and CCl_4. The study specimens were investigated in three states: under a layer of excess solvents, dried in a nitrogen current at 295 K, and produced after heating in a nitrogen current at various temperatures. The experiments performed demonstrated that evolving the aforesaid compounds labeled as R from intercalation compounds of fluorinated graphite in the second stage of saturation with respect to R is kinetically impeded. The rate of deintercalation is particularly low at room temperature. When intercalation compounds of fluorinated graphites with "R compounds" containing C-H bonds are heated to 393-453 K, a gaseous-phase evolution of HF occurs that is accompanied by the appearance of carbon in the solid phase. The evolution of $(CH_3)_2CO^+$ and HF^+ was found to reach significant speeds at temperatures of 353 and 453 K, respectively, which is significantly below the temperature of the initiation of the decomposition of fluorinated graphite (663 K). This fact, coupled with the absence of CF_3^+ ions in the mass spectrum in the specified temperature range, demonstrates that both the evolution of HF and the appearance of a carbon phase are due to the reaction of acetone and fluorinated graphite. Exoeffects accompanied by a rapid mass loss are observed in the temperature range from 423 to 473 K. Figures 4, tables 2; references 10: 7 Russian, 3 Western.

The Catalytic Properties and Composition of the Surface of Films Sputtered From Intermetallic Compounds of Dysprosium and Copper

[Article by K.N. Zhavoronkova and O.A. Boyeva]

UDC 546.01

[Abstract] The authors of the study reported herein examined the specific catalytic activity of DyCu, $DyCu_2$, and $DyCu_6$ films that were sputtered in a vacuum by two techniques. The first technique entailed placing specimens of intermetallic compounds in a tungsten wire spiral, completely vaporizing each specimen for 1 to 7 minutes, and then heating the film specimen at 150°C for over 30 minutes in a vacuum above 10^{-7} torr. The second technique entailed spraying DyCy and $DyCu_6$ specimens sequentially in five to six layers of film each and then cooling the film condensed on the reactor walls with liquid nitrogen to a temperature of -196°C. H_2-D_2 exchange in the temperature range from -196 to -50°C served as the model reaction. This characteristic features of the films' catalytic behavior depending on the composition of the vaporized specimen and the condensation conditions were examined. In the case of films produced by using the first technique, the catalytic activities of the DyCu alloys produced was greater than that of pure Dy; however, the increase in specific catalytic activity differed for each of the individual compounds synthesized. The nature of the temperature dependence of the specific catalytic activity of films sprayed from intermetallic compounds was the same as for films of pure Dy. In other words, there was a sharp bend in the Arrhenius line in the range from -130 to -110°C. Below the sharp bend (region 1), the activation energy amounted to 2 to 3 kJ/mol. Above the sharp bend (region 2), the activation energy of pure dysprosium equaled 6 kJ/mol, whereas that of the alloys (regardless of individual composition) was 13 kJ/mol. At -196°C, the specific catalytic activity of DyCu and $DyCu_2$ films was found to differ by more than two orders of magnitude and was five- to tenfold below the specific catalytic activity of films of $DyCu_6$. In region 2, the values of the specific catalytic activity of films of $DyCu_2$ and $DyCu_6$ differed by a factor of 4.5. Measurements of the specific catalytic activity of films produced by using the second technique were found to coincide with those obtained for DyCu films sputtered in accordance with the first technique. This fact was taken as confirmation of the fact that the contaminated oxidized layer of dysprosium that must necessarily be present on the surface of films sputtered in accordance with the first technique is permeable for hydrogen molecules and that the surface layer corresponding to a Cu:Dy ratio of 1 participates in the catalysis. No segregation was found in the films sputtered by the second technique. The coincidence of the data obtained for the two different spraying techniques further led the authors to conclude that intermetallic compounds are formed even at a temperature as low as -196°C. The study results led the authors to conclude that the catalytic activity in films of Dy and Cu intermetallic compounds develops during the process of condensation of the DyCu intermetallide and that the specific catalytic activity of the resultant film depends on the penetration depth of the formation reaction of the given intermetallic compound. This fact in turn was said

to affect the relationship between the ligand effect and the geometric factor. Figures 4, tables 2; references 11: Russian, Western.

The Structure, Vibration Spectra, and Electric Conduction of $H_4SiW_{12}O_{40} \cdot 8(CH_3)_2SO$ Crystalline Solvate

[Article by Ye.S. Oniani, V.S. Sergiyenko, V.F. Chuvayev, and A.E. Mistryukov, Physical Chemistry Institute, USSR Academy of Sciences, and General and Inorganic Chemistry Institute imeni N.S. Kurnakov, USSR Academy of Sciences]

UDC 548.562;546.776-31

[Abstract] The authors synthesized $H_4SiW_{12}O_{40} \cdot 8(CH_3)_2SO$ crystals. The said crystals were produced from a solvate of 12-silicotungstate with dimethyl sulfoxide [DMSO] and were transparent, colorless, and stable in air. The structural and physicochemical characteristics of the study crystals were determined by the following methods: thermal analysis, electric conduction analysis, x-ray crystallographic analysis, infrared spectroscopy, and proton magnetic resonance spectroscopy. The crystals in question were determined to belong to a monoclinic crystal system with the following nucleus parameters: a = 15.472(4), b = 19.194(5), and c = 22.490(7) angstroms; β = 93.34(2)°; Z = 4; limiting boundary, $P2_1/n$; and R = 0.050 based on 4,267 reflections. The paired protonation of DMSO molecules and the formation of weak H-bonds of the metal groups and oxygen atoms of the heteropolyanion (i.e., heteropolyanion...DMSO-H^+-DMSO...heteropolyanion) were determined to be the driving forces underlying the organization of the study $H_4SiW_{12}O_{40} \cdot 8(CH_3)_2SO$ crystals. The heat stability and electric conduction of the study crystals were each found to be uniquely affected by the specifics of the overall packing of the crystal structure. The desolvation of $H_4SiW_{12}O_{40} \cdot 8(CH_3)_2SO$ was found to begin at temperatures 40 to 60°C lower than the dehydration of $H_3PW_{12}O_{40} \cdot 6H_2O$ and $H_4SiW_{12}O_{40} \cdot 6H_2O$, respectively. An endothermal "order $\rightarrow$ disorder" transition that increases protonic conduction by three orders of magnitude was observed in the study crystalline solvate at 370 K. Figures 3, table 1; references 18: 8 Russian, 10 Western.

Synthesis and Physicochemical Investigation of Binary Hexafluorotitanates of Alkaline Metals

[Article by T.F. Antokhina, T.V. Lysun, V.I. Sergiyenko, T.A. Kaydalova, and I.V. Kiryanova, Chemistry Institute, Far Eastern Department, USSR Academy of Sciences, Vladivostok]

UDC 546.91:548.73:543.422.4:546.821'161:546.31

[Abstract] The authors of the study reported herein have, for the first time ever, synthesized hexafluoro complexes of titanium with alkaline metals. The newly synthesized $NaMTiF_6$ crystals were isolated from solutions with $NaMTiF_6$:M_2TiF_6 ratios of 1:1. Crystal optics studies of the $NaMTiF_6$ microcrystals in convergent polarized light and a study of their extinction revealed that all $NaMTiF_6$ crystals are biaxial and undergo the direct extinction that is characteristic of crystals belonging to a rhombic system, whereas M_2TiF_6 crystals are mean-symmetrical. These conclusions were confirmed by x-ray structural analysis. The similarity of the diffraction patterns and proximity of the parameters of the elementary cells of (1) $NaLiTiF_6$ and $NaLiSiF_6$ and (2) $NaKTiF_6$ and $NaRbTiF_6$ led to authors to conclude that the members of each of these two pairs are isostructural. Finally, the IR absorption spectra of $NaMTiF_6$ photo complexes were measured in the range from 4,000 to 200 cm^{-1}. The results of analysis of these absorption spectra were also in agreement with the crystal optics and roentgenometric data regarding the reduction in the symmetry of complexes' crystalline lattices upon the transition from a homo- to a heteroatomic sublattice. The authors have included tables detailing the results of a chemical analysis of the four aforementioned hexafluoro complexes of titanium and alkaline metals, the parameters of the elementary cells of $NaMTiF_6$, roentgenometric data on $NaMTiF_6$ compounds, and the vibration frequencies of the TiF_6^{2-} ion in binary hexafluorotitanates of alkaline metals as compared with literature data for M_2TiF_6. Tables 4; references 8: 5 Russian, 3 Western.

The Effect of Pressure up to 800 MPa on Solubility in the System Copper Nitrate-Water

[Article by B.R. Churagulov, O.V. Galas, and A.N. Yakushenko, Moscow State University imeni M.V. Lomonosov]

UDC 541.12.034

[Abstract] The authors of this article used the electric conduction and sampling methods to determine the effect of up to 800 MPa of pressure on solubility in the system copper nitrate-hydrogen at temperatures of 298, 323, and 348 K. As their starting substance, the authors used graded-for-analysis $Cu(NO_3)_2 \cdot 3H_2O$ recrystallized from an aqueous solution in the form of crystalline hexahydrate or trihydrate and bidistilled water. The concentration of the copper nitrate solution was determined by iodometric titration with an error of +/-0.1% (by mass). The studies performed indicated that the solubility of $Cu(NO_3)_2 \cdot 3H_2O$ decreases with pressure in

a virtually linear manner. Overall, the change in solubility of $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 6H_2O$ is subject to the same qualitative laws governing other salt-and-water systems. The rate of decrease in solubility of $Cu(NO_3)_2 \cdot 6H_2O$ was found to be much higher than in the case of $Cu(NO_3)_2 \cdot 3H_2O$ and to diminish markedly with pressure. The studies further revealed that the concentration of saturated copper nitrate solutions remains rather high all the way up to 800 MPa. It amounts to more than 3.0 mol/kg H_2O at 298 K. For this reason, concentrated aqueous copper nitrate-based solutions may be used to produce ceramic materials at a pressure of several hundred MPa and temperatures of 298 K and above. Figure 1, tables 4; references 16: 13 Russian, 3 Western.

The Magnetic Susceptibility of $BaCuO_{2+\delta}$ and $Ba_2Cu_3O_{5+\delta}$ in the Temperature Interval From 77 to 300 K

[Article by G.V. Bazuyev, D.G. Kellerman, and V.N. Krasilnikov, Chemistry Institute, Ural Department, USSR Academy of Sciences, Sverdlovsk]

UDC 538.22:546.312

[Abstract] The authors of the study reported herein examined the magnetic susceptibility (χ) of the compounds $BaCuO_{2+\delta}$ and $Ba_2Cu_3O_{5.17}$ in the temperature interval from 77 to 300 K. Their interest in $BaCuO_{2+\delta}$ was the result of its importance in determining the superconductor characteristics of complex barium cuprates and rare earth elements. Their interest in $Ba_2Cu_3O_{5+\delta}$ was due to the fact that it often forms when $BaCuO_{2+\delta}$ is subjected to low-temperature annealing in air or oxygen. The $BaCuO_{2+\delta}$ studied was synthesized in air at 950°C from ultrapure $BaCO_3$ and ultrapure CuO. A mixture of the starting reagents was pressed into disks and roasted for 48 hours. $Ba_2Cu_3O_{5+\delta}$ was produced from BaO_2 and CuO. Carefully ground mixtures of these components (in a 2:3 molar ratio) were pressed and placed in quartz ampules that were evacuated, sealed, and then roasted. The former was roasted for 16 hours at 600°C, and the latter was roasted at 620°C for 36 hours. The ampules were cooled in the furnace. The specimens' magnetic susceptibility was measured by the Faraday method in magnetic fields ranging from 6 to 12 kOe at temperatures ranging from 77 to 295 K. The error in determining χ did not exceed +/-2%. In the case of $BaCuO_{2+\delta}$, the researchers discovered paramagnetic behavior and a large negative temperature-independent component of χ. The magnetic moment associated with the copper ion was found to be higher than the purely

spin value for the Cu^{2+} cation and was found to vary only weakly in the homogeneity range. The magnetic susceptibility of $Ba_2Cu_3O_{5.17}$ was found to obey the Curie-Weiss law with a magnetic moment of 0.90 mb for the copper atom. The study results enabled the researchers to conclude that the appearance of the diamagnetic component of the magnetic susceptibility of $BaCuO_{2+\delta}$ is not related to the presence of $BaCO_3$ or $Ba_2Cu_3O_{5+\delta}$ impurity phases. They further concluded that there is no basis for considering the presence of the tetragonal modification $BaCuO_2$ in the study specimens as the reason for the appearance of a temperature-independent component of magnetic susceptibility. Finally, they concluded that the intermediate nature of the magnetic properties of $Ba_2Cu_3O_{5+\delta}$ (i.e., the reduced values of χ while adherence to the Curie-Weiss law is maintained) is evidently due to the presence in this compound's structure of several exchange reactions of the Cu-positions that all differ somewhat from one another. Figures 2, table 1; references 14: 2 Russian, 12 Western.

Structure Formation and Magnetic Properties of Solid Solutions of Scandium, Titanium, and Vanadium Nitrides

[Article by B.N. Dudkin and Ye.V. Vanchikova, Komi Scientific Center, Ural Department, USSR Academy of Sciences, Syktyvkar, and Syktyvkar State University imeni 50th Anniversary of the Soviet Union]

UDC 546.56

[Abstract] The authors examined the structure formation and magnetic properties of scandium, titanium, and vanadium nitrides. The study compounds were synthesized by nitriding finely dispersed metal powders at temperatures between 1,373 and 1,573 K. Vapor-phase nitrogen and ammonia that had been carefully cleansed of traces of water and oxygen were used as the nitriding agent. According to chemical analysis, the study compounds had compositions of $ScN_{0.8}$, $TiN_{0.9}$, and $VN_{0.9}$, which are all within the range of the said compounds' homogeneity. Solid nitride solutions with a content of 5 to 97 mol% scandium nitride were prepared in accordance with the ceramic technology at 2,073 K for 6 to 8 hours. The homogeneity of the solutions was established by the e-ray phase method. Solutions containing more than 25 mol% dissolved component were classified as heterophase. The composition of the solid solutions was determined by chemical analysis. The studies performed revealed that for solid solutions in the range of both high and low scandium nitride contents, the parameter of the crystalline lattice is virtually independent of the concentration of the solution. In other words, Vegard's law is not fulfilled. Despite the proximity of the effective ionic radii of scandium, titanium, and vanadium and the proximity of the Ne-N bond energies and isomorphicity of the crystalline lattices of the starting nitrides, no continuous series of solid solutions was established in the study systems. Two regions of the homogeneity of solid solutions with a concentration of up to 20 mol% of each component were established. Solutions containing more than 25 mol% dissolved component were classified as heterophase. EPR and NMR studies performed on the solid nitride solutions synthesized established the predominantly metallic nature of the chemical bond. Specifically, the EPR spectra obtained enabled the authors to reject the hypothesis of the presence of strong axial or trigonal distortions of the solid solutions' cubic lattices that would be capable of causing a reduction in the intensity of the NMR signal on account of quadrupole interactions. Rather, the drop in the intensity of the NMR signal from the resonating scandium atoms as the concentration of paramagnetic component in the solid solutions increases was attributed to exchange interactions between the scandium and paramagnetic metal atoms that in turn led to in increase in spin density on the scandium nuclei. This was confirmed by the observation of a sharper drop in the intensity of the [45]Sc NMR signal at low temperatures due to the high localization of the electronic density on the scandium atoms. The appearance of spin density on the scandium atoms was attributed to interactions in the Sc-N-Me and Sc-Me chains. The authors further concluded that the existence of both direct and indirect exchange interactions between metal atoms in the lattice of a solid solution may result in the formation of an overall band structure and an increase in the population of these bands as the concentration of paramagnetic component increases and as the NMR signal attenuates accordingly. Figures 3, table 1; references 8 (Russian).

The Reaction of the Intermetallic Compounds YCo_2, YCo_3, YCo_5, and Their Hydride Phases With Hydrogen in the Presence of Nitrogen

[Article by S.P. Shilkin and L.S. Volkova, New Chemical Problems Institute, USSR Academy of Sciences, Chernogolovka]

UDC 546.3-19'11'17

[Abstract] The authors of the study reported herein examined the reaction of the intermetallic compounds YCo_2, YCo_3, YCo_5, and their hydrides with hydrogen in the presence of nitrogen. The studies were performed with a nitrogen:hydrogen ratio of 1:3, a pressure of 0.25 to 25 MPa, and reaction temperatures of 293 and 723 K. At 293 K, the intermetallides YCo_2 and YCo_3 formed β-hydride phases, whereas YCo_5 formed α-hydride phases. At 723 K the end reaction product in all of the cases studied was a heterophase mixture of yttrium nitride and metallic cobalt. The chemical and phase compositions of the solid reaction products turned out to be identical regardless of whether it was intermetallic compounds or their hydride phases that were brought into contact with the nitrogen-hydrogen mixture. In the gaseous phase products at 723 K, however, up to 7% (by volume) ammonia was discovered in their composite depending on the pressure composition of the intermetallide. The experiments performed confirmed that at room temperature in the pressure interval considered, molecular nitrogen reacts exclusively with the surface layers of the crystalline lattices of the β- and α-hydride phases of intermetallic compounds of the structure YCo_nH_x. Unlike intermetallic compounds formed by yttrium and iron, the reaction of YCo_n intermetallides and their hydride phases with a 1:3 nitrogen-hydrogen ratio at a pressure of 5 MPa and a temperature of 723 K is accompanied by the introduction into the starting alloy matrices of 0.97 to 1.0 nitrogen atoms per formula unit of the compound. The absorption of this amount of nitrogen results in the decomposition of the starting compounds into yttrium nitride and metallic cobalt. The period of the crystalline lattice of yttrium nitride (a = 0.4880 nm) is in good agreement with the literature data,

as are the periods of the crystalline lattice of metallic cobalt (a = 0.2506 and c = 4070 nm). The latter values indicate that metallic cobalt is present in the reaction products in a hexagonal modification. Tables 3; references 5: 4 Russian, 1 Western.

Kinetics of the Reduction of Ni^{2+} by Sodium Dithionite

[Article by Ye.V. Yegorova, S.V. Makarov, Ivanovo Chemical Technology Institute and Tashkent Textile and Light Industry Institute]

UDC 541.124:546.742:546.223.1

[Abstract] A number of publications have examined the reduction of dithionite complex ions of various metals. No data are available on the kinetics of the reduction of noncomplexed metal ions, however. In view of this fact, the authors of the study reported herein studied the kinetics of the reduction of a Ni^{2+} ion by sodium dithionite in aqueous buffer solutions. $Na_2S_2O_4$ with a grade of pure and $NiCl_2 \cdot 6H_2O$ with a grade of chemically pure were used. $NiCl_2$ was reacted with $Na_2S_2O_4$ with a 20- to 50-fold excess of reducing agent and constant ionic solution strength (μ) (KCl, 0.2 mol/l). The reaction was halted at specified intervals by adding an excess of formaldehyde. The sediment was centrifuged out and dried. The NiS was then dissolved by adding 2 N HCl, and the sulfide was determined by the iodometric method. The Ni^{2+} concentration was determined by complexonometric titration, and the amount of nickel formed was determined from the material balance. The $S_2O_4{}^{2-}$ was analyzed iodometrically in accordance with the familiar method. The experiments established that, besides reducing, the Ni^{2+} ions also react with one of the products of the decomposition of sodium dithionite, i.e., the sulfide ion. This reaction results in the formation of NiS. Even in the presence of significant dithionite surpluses, the total reduction of Ni^{2+} could not be achieved. This was attributed to the fact that the rate at which $Na_2S_2O_4$ decomposes at a pH of 4.00 and a temperature of 295 to 323 K is significantly faster than the reduction rate. The experiments also established that the role of the reduction route involving the ion-radical $S \cdot O_2{}^-$ increases as the reaction temperature rises. The contribution of the said route to the total rate of the reduction process decreases, however, as the $[S_2O_4{}^{2-}]_0/[Ni^{2+}]_0$ (where $[Ni^{2+}]_0$ is the initial concentration of Ni^{2+} and where $[S_2O_4{}^{2-}]_0$ is the initial sodium dithionite concentration) ratio decreases. Formulas for determining the contributions of the said ion-radical and $S_2O_4{}^{2-}$ were derived. The authors also succeeded in deriving an equation for the rate of the reduction reaction that satisfactorily describes the experiment data. Figures 2, tables 2; references 14: 4 Russian, 10 Western.

Change in the Properties of $LaNi_5$ During Repeated Formation and Decomposition of the Hydride Phase

[Article by V.Z. Mordkovich, N.N. Korostyshevskiy, Yu.K. Baychtok, V.P. Mordovin, N.V. Dudakova, and M.Kh. Sosna, State Scientific Research Institute of the Nitrogen Industry, Moscow]

UDC 546.3

[Abstract] Existing publications regarding the behavior of $LaNi_5$ during the repeated formation and decomposition of a hydride phase are contradictory. One general conclusion that can, however, be drawn from the existing literature is that the cyclic formation and decomposition of a hydride phase results in the gradual pulverization of the specimen and expansion of the lines on x-ray diffractograms. This in turn indicates a reduction in the dimensions of the crystallites and, possibly, the significant accumulation of defects and stresses. In view of these facts, the authors of the study reported herein performed their own study of the change in the properties of $LaNi_5$ that occurs upon repeated formation and decomposition of a hydride phase. They used type A commercial-grade hydrogen and ultrapure hydrogen obtained by diffusion through palladium alloy membranes. The $LaNi_5$ was prepared by using calcium hydride to reduce nickel and lanthanum oxide powders. An automatic experimental unit consisting of a stainless steel reactor connected to a pressure gauge, buffer tank, and shutoff valve was designed and constructed for the experiments. Preactivated specimens were placed in the reactor, which was filled with hydrogen at room temperature (T_0) to the specified initial pressure (P_1). The reactor was then heated to a specified temperature (T_1), and the pressure was raised to a specified pressure (P_2). The pressure returned to its initial value as the specimen was cooled. The drift of P_1 and P_2 was monitored during the course of the experiment, and the specimen's hydrogen capacity was measured periodically (hydrogen was evolved from the specimen at 150°C). The water displacement method was used to measure the volume of evolved hydrogen. At the end of the experiment the specimen was unloaded from the reactor in an inert atmosphere and subjected to x-ray phase analysis on a DROP-3 diffractometer. The cooling time was set between 100 and 120 seconds, and the cycle time was set between 300 and 450 seconds. The results of an experiment with a specimen having the composition $Ce_{0.5}La_{0.5}Ni_5$ revealed that a reduction in hydrogen capacity becomes noticeable after several hundreds of cycles. Statistical processing revealed that the reduction in hydrogen capacity can (with a confidence limit of 0.9) be described as a first-order process, with a 50% capacity loss occurring at a T_1 of 150°C after 6,300 +/- 800 cycles or at a T_1 of 100°C after 85,000 +/- 10,000 cycles. These results led the authors to conclude that reducing the decomposition temperature significantly

slows the degradation process of the intermetallic compound. The irreversible loss of hydrogen capacity on the part of the study intermetallic compound that was discovered was attributed to a hydrogenolysis reaction. The recoverable loss found was attributed to the formation of an $LaNi_5H_{3-4}$ hydride phase in a kinetically inhibited form. The irreversible loss that was found to occur at 150°C after 5,400 cycles amounted to 25%, whereas the irreversible loss occurring at a decomposition temperature of 100°C after 6,700 cycles amounted to 3.5%. Figures 5; references 20: 15 Russian, 5 Western.

The Structure and Role of HF Sorption Complexes in the Fluorination of a Silica Surface

[Article by V.M. Gunko, Ye.F. Voronin, and A.A. Chuyko, Surface Chemistry Institute, UkSSR Academy of Sciences, Kiev]

UDC 541.183

[Abstract] The authors of the study reported herein used the MNDO method to perform a detailed quantum chemical examination of the mechanism of the reaction of hydrogen fluoride molecules with surface silanol groups. A fragment of a silica surface was modeled by the cluster $[(AO)_3SiO]_3SiOH$, where A represents Is pseudoatoms, based on the structural motifs of β-cristobalite with topological disordering of the atoms in the side prisms and subsequent optimization of the cluster's geometry by eliminating the lengths of the O-A bonds. In other words, amorphous SiO_2 was modeled with its short-range order preserved. On the basis of a quantum chemical analysis of their own model and data from previous experimental studies, the authors established that the fluorination of a silicon surface by hydrogen fluoride from the gaseous phase occurs through several stages of the formation and transformation of a number of surface sorption complexes. These complexes include $\equiv$Si-OH groups and HF molecules. A four-center complex that simultaneously contains a silicon-fluorine donor-acceptor bond and an H_F-O_{SiOH} hydrogen bond corresponds to the intermediate. They further determined that the formation of such a complex is more favorable from an energy standpoint when the hydrogen bond is formed first and is then followed by formation of the donor-acceptor bond. Further interaction of the surface four-center complex with HF or NH_3 molecules as a result of proton transfers was found to result in destruction of the complex and formation of the reaction's end products. Calculation of the proton transfer occurring in the complex $NH_3 \cdot HF$ in the gaseous phase resulted in an activation energy of about 250 kJ/mol; however, the presence of several water molecules was found to facilitate the virtually barrier-free formation of a solvated ion pair. The activation energy of the H^+ transfer in the said complex on an SiO_2 surface was less
than in the gaseous phase by a factor of 2.5; however, the presence of several polar molecules on one SiO_2 active center was found to result in a further reduction in the barrier height as is the case in liquids. An increase in the polarity of the HF molecule and the loosening of the F-H bond in a complex involving ammonia coupled with a simultaneous growth in the activation of H^+ transfer to the O atom through NH_4^+ was found to increase the probability of H^+ tunneling through barrier G. These and other calculations enabled the authors to establish that the NH_3 (or some other base) molecule plays two roles: Not only does it increase the polarity of the F-H bond, which loosens as the strength of the F $\rightarrow$ Si bond increases, but it also increases the likelihood of H^+ tunneling due to an increase in the critical value of the half-width of the barrier G (d_t). The results obtained are in agreement with experimental data regarding an increase in the dissociation constants of protolytic molecules in the adsorption layers on an SiO_2 surface and protonic conduction. Figures 4, table 1; references 21: 19 Russian, 2 Western.

Reactions of Implantation Into P-Hlg Bond in Phosphoranes. The Synthesis of 1-Halogenalkoxyphosphoranes

[Article by V.F. Mironov, T.N. Sinyashina, Ye.N. Ofitserov, F.Kh. Karatayeva, P.P. Chernov, I.V. Konovalova, and A.N. Pudovik, Kazan State University imeni V.I. Ulyanov-Lenin]

UDC 547.26'118

[Abstract] The authors of the study reported herein have proposed and implemented an approach to synthesizing functionally substituted 1-halogenalkoxyphosphoranes by reacting cyclic, bicyclic, and acyclic mono-, di-, and trihalogenphosphoranes with chloral and bromal. During their study, the authors synthesized 49 different compounds. Fourteen of the reactions are detailed at the end of the study. Because the occurrence of stable phosphoranes is most easily observed for phosphorus (V) halides containing a dioxaphospholane cycle, the authors began by reacting them with dibromophosphorane aldehydes based on 2-(2,2,3,3-tetrafluoropropoxy)-, 2-(2,2-dibromovinyloxy)-, and 2-fluoro-4,5-benzo-1,3,2-dioxaphospholanes as the most stable of the known dibromophosphoranes. Choral and bromal were complexed with dibromophosphorane to form products with 1:1 and 1:2 ratios. Several thick and glassy stable phosphoranes, thick nonredistilled liquid phosphoranes, and crystalline phosphoranes that proved to be stable in an inert atmosphere were then isolated. The yield of several of the phosphoranes and one of the spirophosphoranes synthesized was found to increase upon protracted holding of monobromophosphorane in solvent at

20°C. The reaction of bis(pyrocatechin)monochlorophosphorane with CZ_3CHO aldehydes did not result in any products of complexing along the carbonyl group. Instead the starting phosphorane turned into bis(pyrocatechin)pyrocatechinphosphorane. Two dibromophosphoranes were also found to form complexes with bromal and chloral and form glassy phosphoranes that are readily soluble in organic solvents. Unlike the P-Br bond in the said compounds, the P-F bond did not split under the effect of aldehydes. Other acyclic dibromophosphoranes were found to form a complex with chloral at the carbonyl group and form 1-bromoalkoxyphosphoranes (such as difluorophosphorane). In addition to cyclic, bicyclic, and acyclic relatively stable mono- and dibromophosphoranes, pyrocatechintrihalogenphosphor was also found to form in a reaction with trihalogenacetaldehydes. The reaction of pyrocatechintrichlorophosphorane with selected aldehydes was found to occur significantly more slowly than many of the other study reactions and manifested stage-by-stage complexing. This enabled the authors to propose a staged complexing process that proceeds through the initial attack of the aldehyde's oxygen atom to the phosphorus atom that is lacking an electron. Included among the other compounds synthesized are spirophosphoranes that arise as a result of the disproportionation of two of the phosphoranes synthesized. Amidophosphate (the 49th and final compound synthesized) was postulated to be formed through ligand exchanged in a quasi-phosphonium salt (L) that turns into an H salt, which in turn was said to easily decompose into phosphate and tribromoethylene (the structure of which was confirmed spectrally). Data from ^{13}C, ^1H, ^1H-$[^{31}P]$ NMR studies of a number of the compounds synthesized are presented in table form along with data on the chemical shifts and element analysis of several of the compounds. Figures 3, tables 3; references 24: 7 Russian, 17 Western.

The Cyclic Attachment of Nitrile Imines to Allenyl and Propinyl Phosphonates

[Article by N.G. Khusainova, Yu.G. Trishin, E.A. Irtuganova, L.A. Tamm, V.N. Chistokletov, and A.N. Pudovik, Kazan State University imeni V.I. Ulyanov-Lenin]

UDC 547.341

[Abstract] The literature does not contain any descriptions of reactions of nitrile imines activated by a phosphoryl group. In an effort to fill this gap, the authors of the study reported herein examined the cyclic attachment reaction of 1,2-propadiene phosphonates with C-substituted N-arylnitrile imines to allenyl phosphonates. Equimolar quantities of allenyl- and propinyl phosphonates and nitrile imines were added to a solution of

unsaturated phosphonate and hydrazidoyl chloride in benzene. A twofold excess of triethylamine was added, and the reaction mixture was heated for 25 to 30 hours at a temperature of 70 to 90°C until the absorption bands of the respective multiple bond (either C=C or C=C=C) in its infrared spectrum disappeared. The hydrochloric triethylamine residue was then filtered off, the solvent was removed in a vacuum, and the residue was distilled or else subjected to chromatographic analysis. Chloroform and hexane in a 3:1 ratio served as the eluent. The cyclic attachment of C-substituted N-arylnitrile imines to allenyl phosphonates was found to occur along the 1,2-double bond of cumylene and to involve the formation of a mixture of regionally isomeric pyrazoles. The reaction of nitrile amines with propinyl phosphonates, on the other hand, was found to occur with regional selectivity. Overall, both allenyl and propinyl phosphonates manifest a low degree of activity in reactions with nitrile imines. Between 27 and 30 hours of heating at a temperature of 70 to 80°C was required for the complete disappearance of the characteristic absorption bands of dipolarophils $[v(CH=C=CH_2$ and $v(C=C)]$ in the infrared spectra of the reaction mixtures. Table 1; references 7: 5 Russian, 2 Western.

The Reaction of 2,2,2-Trichloro-4,5-Benzo-1,3,2-Dioxaphospholane With Disilylated Amides of Acetic, Phosphoric, and Sulfo Acids

[Article by M.A. Pudovik, L.K. Kibardina, and A.N. Pudovik, Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan Affiliate, USSR Academy of Sciences]

UDC 547..1'128'118

[Abstract] The authors of the study reported herein reacted 2,2,2-trichloro-4,5-benzo-1,3,2-dioxaphospholane with distilled amides of acetic, phosphoric, and sulfo acids. They discovered that at room temperature, the reaction of phosphorane with N,N-bis(trimethylsilyl)-acetamide in ether forms not acetylimidochlorophosphate but rather 2-chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane. This is explained by the fact that the imidochlorophosphate formed in the first stage during elimination of the acetonitrile is rapidly transformed into dioxaphospholane. Using a twofold excess of silylamide was found to result in 2-trimethylsiloxy-2-oxo-4,5-1,3,2-dioxaphospholane. Chlorophosphate, the intermediate product, was discovered to react with the second silylamide molecule to form silylamidophosphate. Upon the β-decay of its tautomeric imide form, the latter is transformed into the end product siloxycyclophosphate. Because this type of elimination is only known to exist in a number of P (III) derivatives, the authors conducted a separate study of the reaction of chlorophosphate with silylamide. ^{31}P NMR spectra of

the reaction mixture established the intermediate formation of silylamidophosphate, which was transformed into siloxyphosphate upon distillation. The reaction of phosphorane with N,N-bis(trimethylsilyl)benzenesulfamide was unexpectedly found to result in the formation of cyclic chlorophosphate. ^{31}P NMR spectroscopy data confirmed that only slight amounts of imidochlorophosphate are present in the reaction mixture. The authors' overall conclusion from the studies performed was that the reaction of 2,2,2-trichloro-4,5-benzo-1,3,2-dioxaphospholane with distilled amides of acetic, phosphoric, and sulfo acids results in the evolution of trimethylchlorosilane and the formation of N-substituted imidochlorophosphates that are generally unstable and undergo a β-decay. This β-decay in turn results in the formation of acid chlorides with a phosphorus atom that has a coordination number of 3 or 4. References 9: 6 Russian, 3 Western.

Anhydrous Derivatives of Trivalent Phosphorus Acids Containing a Cyano Group

[Article by A.N. Pudovik, V.N. Nazmutdinova, and L.P. Chirkova, Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan Scientific Center, USSR Academy of Sciences]

UDC 547.1'118

[Abstract] In a previous communication, the authors of this study reported that the reaction of dicyanides of P (III) with hydrogen chloride results in the formation of phosphorus chlorocyanides. Upon heating and storage, the said compounds were found to disproportionate into their respective dichlorides and dicyanides. An analogous tendency toward disproportionation was observed for the acylcyanophosphites trifluoro- and trichloroacetylcyanophosphite and pivaloyl- and isobutyrylcyanophosphite. The disproportionation of all of these compounds appeared to proceed in accordance with the same mechanisms. This line of research is continued in the present article. In accordance with literature data on the geometry and energy of the bonds of selected esters and cyanides of trivalent phosphorus, the authors have proposed a scheme for the disproportionation of O-acylcyanophosphites that includes the cyclic transfer of electron density in a transition state A. They further hypothesized that the situation would change radically if the heteroatom E = S. Their hypothesis was based on the fact that the opening of the C=O bond should entail the formation of a thiocarbonyl group, the breaking of the P-S bond, and the formation of a P-O bond. In fact, the reaction of dicyanides of trivalent phosphorus with thioacetic acid in a 1:1 ratio was found to result in the formation of thermally stable S-acetylcyanothiophosphites and -phosphonites. The structure of the said compounds was confirmed by infrared, ^{31}P NMR, and

^1H spectroscopy, and their composition was confirmed by elementary analysis. Alcoholysis of S-acetylcyanothiophosphite at room temperature was found to be accompanied by the formation of O,O-diethyl-S-acetylthiophosphite. When the temperature was lowered (to between -20 and -30°C), the said reaction was found to result in diethylcyanophosphite. References 15: 10 Russian, 5 Western.

The Reaction of Cyclic Incomplete Esters of Phosphorous Acid With Enamines—An Electrophilic Variation of Pudovik's Reaction

[Article by Yu.G. Safina, G.Sh. Malkova, and R.A. Cherkasov, Kazan State imeni V.I. Ulyanov-Lenin]

UDC 547.26'118

[Abstract] It has been demonstrated elsewhere that cyclic incomplete esters of phosphorous acid are capable of attachment along C=C bonds activated not only by electron-acceptor but also by electron-donor substituents. In a number of unsaturated compounds, these bonds are characterized by a very high degree of activity in reactions of the attachment of cyclophosphites. Such reactions represent a variation of Pudovik's reaction that has not been studied adequately. Moreover, reactions involving enamines have only been mentioned in several cases. In view of these facts, the authors of the study reported herein examined those reactions of five- and six-membered cyclic incomplete phosphites with enamines in which the multiple bond possesses different degrees of nucleophilicity. The different nucleophilicities were obtained by adding electron-donor and -acceptor substituents to the bond and to the nitrogen atom of the amino group. Reactions involving acyclic incomplete phosphites were also studied for the sake of comparison. The reactions studied were found to occur in two main stages: The cyclophosphites are initially attached at the C=C multiple bond of the conjugate system N-C=C-C+) of enaminoketones. This then results in the formation of bis-phosphorylated derivatives. The experiments performed established that cyclophosphorous acids manifest a strong tendency toward reactions of noncatalyzed electrophilic attachment to enamines. The reactivity of the latter was determined to be largely dictated by the extent to which the electron density is localized at the C=C bond. Two factors in particular were determined to reduce the activity of the unsaturated partner in the said attachment reactions: (1) the reduction of the amino group's electron-donor capability during the transition from a tertiary to a primary amine and (2) the addition of α- and β-electron-acceptor or β-electron-donor substituents to the multiple bond. In these cases, however, the reactivity of all of the enamines examined remains rather high. It is for this reason that processes involving enamines may be used successfully

to synthesize functionally substituted α-aminophosphoryl compounds. Tables 4; references 33: 24 Russian, 9 Western.

Kinetics of Reactions of Hydrazides of Diarylphosphinic Acids With Phenyl Isothiocyanate in Benzene

[Article by N.I. Yanchuk, Ternopol State Pedagogical Insitute imeni Ya.A. Galan]

UDC 547.234.1+547.241+541.127

[Abstract] The authors of the study reported herein examined the general kinetic laws governing the reactions of hydrazides of diarylphosphinic acids with phenyl isothiocyanate in benzene at different temperatures. They also studied the effect of structural factors in a molecule of hydrazide of diphenylphosphinic acid and the effect of temperature on its reactivity. The hydrazides of diarylphosphinic acid used in the experiments were synthesized from the respective acid chlorides and hydrazine-hydrate in accordance with methods described elsewhere. The phenyl isothiocyanate was distilled in a vacuum directly before use. The experiments were repeated in series of three each and included six to eight measurements. A transformation depth of at least 80% was achieved in all cases. The kinetics of the reactions of the formation of phosphorus-containing semicarbazides was studied at temperatures of 298, 313, and 328 K, and the familiar formulas were used to calculate the reactions' activation parameters. The confidence limit of the experiments was calculated at 0.95. The effect of substituents on the reactivity of hydrazides of diarylphosphinic acids was found to be described by Hammett's equation using $\sigma^\oplus$ constants. The effect of substituents at the phosphorus atom was found to be additive. The absolute value of the reaction constant ρ was determined to be -0.509 at 25°C. This was taken as confirmation of the low sensitivity of the study reaction series to structural changes in the molecule of diarylphosphinic acid hydrazide (as was also observed early in reactions with phenylisocyanate (ρ = -0.260) and picrylchloride (ρ = -0.317). The weakening of the electronic effect of the substituents in the hydrazide nuclei on the reaction center was linked with the electron-isolating effect of the PONH group. At all of the temperatures studied, the logarithms of the rate constants of the study reaction were found to be in good agreement with the $\sigma^\oplus$ constants of substituents at the phosphorus atom of hydrazides. The experiments conducted also confirmed the existence of an isokinetic relationship in the system studied. The isokinetic temperature in the reaction series studied was determined to equal 487 +/- 11. Because the isokinetic temperature found was far above the temperature range studied, it could not be verified experimentally in the research reported here. The change

in activation enthalpy ($\beta > T_{exp}$) was found to be the predominant factor in the change in reactivity of the hydrazide of diarylphosphinic acid induced by substituents. In other words, the reaction series studied was found to be characterized by enthalpy control of reactivity. Tables 5; references 27: 21 Russian, 6 Western.

The Synthesis of New Functionalized Complexing Agents Based on Phenylhydrophosphinyl Derivatives of Crown Ethers

[Article by V.I. Kalchenko, N.A. Parkhomenko, O.A. Aleksyuk, and L.N. Markovskiy, Organic Chemistry Institute, UkSSR Academy of Sciences, Kiev]

UDC 547.26'118

[Abstract] The functionalization of crown ethers by exocyclic phosphsorus-containing groupings makes it possible to create effective new complexing agents, extractive reagents, solubilizers, polymer sorbents, and interphase and metal cluster catalysts. In view of the great promise of this area of research, the authors of the study reported herein worked to develop new methods of synthesizing (1) macrocyclic polyhedral complexing agents with functional exocyclic groupings and (2) bis-crown-ethers by proceeding from two benzo crown ethers containing reactive phenylphosphonoyl groupings in their benzene rings. All of the study reactions were performed in an atmosphere of dry argon. Phenylphosphonoylbenzo-15-crown-5 was found to attach easily to the C=N bond of 1-phenoxy-2,2,2-trichloroethylisocyanate in the presence of catalytic quantities of triethylamine to form 4-[phenyl(N-1-phenoxy-2,2,2-trichoroethylcarbamoyl)phosphoryl]benzo-15-crown-5. The starting crown ethers were also reacted with 2-bromoethanol in dimethylsulfoxide in the presence of aqueous potassium hydroxide to form macrocyclic phosphine oxides containing reactive 2-hydroxyethyl groupings. Phenylphosphonoylbenzo-15-crown-5 was then reacted with 11-bromo-1-undecene to form a macrocyclic with a peripheral C=C bond. Depending on the reaction temperature used, reacting a benzo crown ether with allyl bromide resulted in the formation of products containing both allyl and 1-propenyl radicals at the phosphorus atom. At 20°C, the said reaction resulted in the formation of bis(allylphenylphosphoryl)dibenzo-18-crown-6 in a 65% yield. When the same reaction was conducted at 45-50°C, bis(1-propenylphenylphosphoryl)dibenzo-18-crown-5 was formed with a 60% yield. Isomerization of bis(1-propenylphenylphosphoryl)dibenzo-18-crown-5 in the presence of catalytic quantities of sodium ethylate

resulted in yet another new compound, i.e., 4,4'(5')-bis(1-propenylphenylphosphoryl)dibenzo-18-crown-6. The reactions resulting in the aforementioned and other new crown ether derivatives are described in detail. References 13: 7 Russian, 6 Western.

The Reaction of Organic Arsenic Derivatives With Picric Acid in CCl₄

[Article by V.V. Yakshin, A.I. Zarubin, I.A. Komolova, Ye.K. Ryabova, and F.M. Ilyukova, All-Union Scientific Research Institute of Chemical Technology, Moscow]

UDC 541.427.549

[Abstract] Organic arsenic oxides R_3AsO in anhydrous media possess the properties of rather strong bases. Their ability to form strong complexes with salts of a number of metals may be used in extraction processes. In view of this fact, the authors of the study reported herein examined the reaction of organic derivatives of arsenic with picric acid in CCl_4. Oxides of tertiary arsines were synthesized, purified, and dried as published elsewhere. A solution of R_3AsOO in CCl_4 with a concentration of 10^{-3} mol/l was placed in a 25-ml glass cell. The picric acid solution used as a titrant was added to the cell automatically with a dosing precision of 0.004 ml. The error in measuring the enthalpy of association (ΔH_{298}^0) was determined to equal +/-1.5 kJ/mol. The equilibrium constants were calculated based on the results of spectrophotometric measurements taken on an SF-20 spectrophotometer in the wavelength range from 340 nm to 450 nm with an incandescent lamp serving as the radiation source. The experiments conducted revealed that the protonation of arsine oxides of picric acid in CCl_4 results in the formation of two complexes: $[BHB]^+A^-$ (when $c_{HA}/c_B = 0.5$) and BH^+A^- (when $c_{HA}/c_B = 1$). The formation of both of these complexes was confirmed spectrophotometrically. The authors noted that the molar extinction of picrate in BH^+A^- complexes (which are formed by relatively weak electron donors) is much lower than in complexes of strong bases. This was attributed to the different degrees of proton transfer from picric acid to the arsine oxide group of the base (the degree of proton transfer naturally decreases as the strength of the base decreases). The association enthalpies found for the complexes were in good agreement with the sum of the Taft induction constants of the substituents for the case of an arsenic atom. The authors found a linear relationship between the enthalpy of association (ΔH_{298}^0) and the entropy of formation (ΔS_{298}^0) (r = 0.095). In order of basicity with respect to picric acid in CCl_4, the arsine oxides studied may be ranked as follows: $(C_8H_{17})_3AsO > iso-(C_5H_{11})_3AsO > cyclo-(C_6H_{11})_3AsO > (C_{12}H_{25})_3AsO > (C_8H_{17})_2AsO(C_6H_5) > (C_8H_{17})_3AsO(C_6H_5)_2 >$

$(C_6H_5)_3AsO$. This ranking is in good agreement with a previously published basicity series. Figures 2, table 1; references 7: 5 Russian, 2 Western.

The Reaction of N-Aminoalkylated Oxazaphospholane With Ethanolamine and o-Aminophenol

[Article by M.A. Pudovik, S.A. Terentyeva, and A.N. Pudovik, Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan Scientific Center, USSR Academy of Sciences]

UDC 547.794.2'118

[Abstract] The authors of this letter to the editor report finding that the reaction of 2-diethylamino-3-diethylaminomethyl-4,5-benzo-1,3,2-oxaza-phospholane (I) with ethanolamine and o-aminophenol results in the formation of two spirophosphoranes. The first stage of the said reaction is said to entail alcoholysis of the exocyclic P-N bond of I and to result in a cyclic phosphite. Subsequent N → P migration of the aminomethyl group results in the formation of a cyclic imidophosphonate that is in turn stabilized by intramolecular attachment of an amino group at the P=N double bond. The chemical shifts of the phosphorus nuclei of the spirophosphoranes formed are reported to equal -32 and -26 ppm, respectively. The procedures used in implementing the above reactions are detailed.

The Reaction of 2-Acetoxy-4,5-Benzo-1,3,2-Dioxaphospholane With Compounds Containing an N-Si Bond

[Article by M.A. Pudovik, L.K. Kibarbina, and A.N. Pudovik, Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan Scientific Center, USSR Academy of Sciences]

UDC 542.91:547.26'118

[Abstract] The authors of this letter to the editor report finding that the exothermal reaction of 2-acetoxy-4,5-benzo-1,3,2-dioxaphospholane (I) with trimethylsilyldiethylamine results in the formation of 2-diethylamino-4,5-benzo-1,3,2-dioxaphospholane (II) (δ_P, 150 ppm). They further report that the reaction of I with N,N-bis(trimethylsilyl)acetamide results only in silylphosphite, whereas the reaction of I with N-trimethylsilylacetamide results in both silylphosphite and a small amount of 2-acetamido-4,5-benzo-1,3,2-dioxaphospholane (δ_P, 134 ppm). The procedures used in implementing these reactions are detailed. References 2 (Western).

Complex Technology of Enrichment of Coal Sludges

927M0009A Moscow KOKS I KHIMIYA in Russian No 7, July 1991 pp 5-6

[Article by L. L. Korsak, N. A. Krasnikova and Ye. K. Samoylova;]

[Abstract] Development of a centrifugal-gravitational technology which reduces sulfur content in flotation feeding and loss of combustible mass with wastes was discussed. Laboratory studies and industrial tests of a modernized spiral classifier were used to develop a complex technology of enrichment of primary slimes in the spiral classifier and by flotation. Three variants of the complex technology of enrichment were worked out during operation of the classifier in a classification regime, in an enrichment regime with separation of 2 products and in an enrichment regime with separation of 3 products. Use of the "complex" technology variant produced: an increase of yield of concentrate in comparison with the base figure by 0.6 percent; reduction of sulfur content of the total concentrate by 0.29 percent (abs); decrease of loss of combustible mass with wastes and reduction of flotation volumes (by 30 percent) and circulating loadings. Introduction of the complex technology at TsOF "Kiyevskay" produced an economic impact of the order of 200,000 rubles per annum. Figure 1.

New Method of Introducing Fusing Additions Into Charge

927M0009B Moscow KOKS I KHIMIYA in Russian No 7, July 1991 pp 10-11

[Article by I. T. Selyanko, P. V. Karnozhitskiy, V. I. Romas et al.;]

UDC 662.741.3.022.001.5

[Abstract] A new method of introducing fusing additions which ensures their uniform distribution throughout the charge at any softening point permits the use of residual petroleum products without additional "redivision" as fusing additions. The method involves loosening of the freely falling flow of the charge and dispersion of the liquid-like additions in a combined procedure. Results of processing a charge on an experimental-industrial device of uniform distribution of the addition with productivity of about 3 tons per hour with subsequent coking in a 300-kg furnace at the Kharkov Experimental Coking-By Product Plant were presented and discussed. Use of the device promoted uniform distribution of the fusing addition in the flow of the charge and made it possible to use petroleum products with softening point less than 100 degrees C. Use of the device reduced the cost of the process of introducing the fusing additions and decreased its expenditure. The annealed charge yielded coke with strength indicators equalling those of standard coke. Figure 1; references 5 (Russian).

Combining Ammonia and Cyanides in Ammonia Waters by Formaldehyde

927M0009C Moscow KOKS I KHIMIYA in Russian No 7, July 1991 pp 24-25

[Article by N. Kh. Ckerkasov, T. N. Ovodkova, V. G. Telegin and V. R. Rachkov; Nizhnetagilskiy Metallurgy Combine]

UDC 662.764.074.34'39

[Abstract] Results of laboratory studies of binding of ammonia by formaldehyde, performed at the Nizhnetagilskiy Metallurgy Combine in 1989 to reduce the free ammonia content in sewage, were presented. The study considered the nature of reactions occurring during such binding, the composition of the products being obtained and the "competition" of reactions occurring for such a complex system as ammonia waters of the coking by-product industry. The use of methanol-free formalin in the experiments prevented emulsification of oils and resins after introduction of formaldehyde. The laboratory studies resembled the situation existing under industrial conditions. Removal of ammonia and cyanides required a larger quantity of formalin and the reaction of formaldehyde with ammonia may compete with the reaction of formaldehyde with cyanide. The formaldehyde content in the final cooling cycle must be controlled at pH 7.4-7.5 to prevent appearance of free formaldehyde. Figure 1.

Intensification of Heat Exchange and Mass Exchange Processes

927M0009D Moscow KOKS I KHIMIYA in Russian No 7, July 1991pp 31-32

[Article by P. D. Redka; Donetsk Coking By-Product Plant and Ye. V. Brodskiy; Donetsk Chemico-Technological Institute]

UDC 662.74:66.021.4:622.276.6

[Abstract] The Donetsk Coking By-Product Plant and the Donetsk Chemico-Technological Institute have collaborated on development of highly efficient heat exchange and mass exchange equipment. Intensification is achieved by increase of the rate of material flows and increase of the interphase contact surface in the use of different types of dispersing devices and also bubbling devices which ensure interaction of phases in the gas-liquid layer of a height up to 300 mm. The collaboration has produced a direct flow contact device for a phenol extracting column of the Rutchenkovskiyy section which increased the efficiency of removal of phenols from ammonia water and a 1200 mm diameter gasoline column with foam-eddy plates which increases production of gasoline while reducing steam expenditure on distillation and elimination of 2 of the operating gasoline scrubbers. The Donetsk section is preparing a 600 mm ammonia scrubber with throughput of up to 12-15 m^3 of

water per hour and installation of non-packing gasoline scrubbers with plates and dispersion devices intended for repeated dispersion of absorption oil in equipment without use of a pump. The Smolyaninovskiy Coking By-Product section is developing a 1200 mm ammonia scrubber and a 1000 mm diameter ammonia column with throughput of up to 20 m³ of water per hour with eddy modules which can operate in regimes for emulsion or dispersion of a liquid by a gas flow and in a regime of separation of phases after their interaction.

Determination of Moisture Content of Coke By Neutron Hygrometer

[Article by V. M. Strakhov, M. B. Shkoller, L. V. Kopeliovich et al.]

[Abstract] Studies performed at the coking by-product factory of the Kuznetsk Metallurgical Combine compared the moisture content of 42 samples of blast-furnace coke by the gravimetric method and by use of a neutron hygrometer. Under actual production conditions the readings received by the neutron hygrometer were not as accurate as those obtained by the gravimetric method. Results obtained by the neutron hygrometer proved to be in error by as much as 2-4 percent. The error was attributed, in part, to the effect on hygrometer readings of the nuclear-physical properties of dry coke (its capacity to absorb and moderate neutrons). These properties of coke depend upon the content of hydrogen, iron, boron, cadmium and other elements in it. The properties of coke from different parts of the coke clinker may differ greatly and distort neutron hygrometer readings. The use of neutron hygrometers to calculate quantities of coke fed into blast furnaces, without modification, was not justified.

Membrane Separation of Hydrocarbons of Associated Petroleum Gas

[Article by N.E. Kalyuzhnyy, V.M. Sidorenko, S.M. Shishatskiy, and Yu.P. Yampolskiy, Petrochemical Synthesis Institute imeni A.V. Topchiyev, Academy of Sciences, Moscow, and Polimersintez Scientific Production Association, Vladimir]

[Abstract] Great progress has been achieved in membrane gas separation in the past 10 years. It has become a competitive commercial gas separation technology, but its use is still limited to separating the components of air, isolating hydrogen from mixtures of hydrogen with nitrogen, methane, and carbon oxide; and separating mixtures of CO_2 with CH_4 and He with CH_4. In a continuation of this line of research, the authors of the study reported herein studied the membrane separation of hydrocarbons of associated petroleum gas. Specifically, they studied the permeability of films and membranes based on the siloxane-containing block copolymers silar and carbosil with respect to the individual hydrocarbons C_1 through C_4 and their mixtures. Mass spectrometric and volumetric measurements of the permeability of the individual gases and binary and multi-component hydrocarbon mixtures confirmed that control of the membrane concentration of the components and control of the composition of the petroleum gas would indeed be possible. The data obtained were used to design a gas separation unit to prepare fuel gas whose n-pentane content only needed to be reduced to 0.5 volume percent. They calculated the composition (volume percent) of the products of the membrane separation of petroleum gas on a membrane with a surface of 510 m². In the separation process designed, petroleum gas enters a gas engine compressor via a pipeline at a pressure of 14 atm and a temperature of 20°C. A portion of the gas is withdrawn for use as fuel for the compressor's motor and is fed to the membrane gas separation unit, at which point it is separated into two approximately equal flows. The retained product (containing 0.5% n-pentane by volume) is fed into the compressor's drive motor. The permeated product (which is enriched in heavy C_3-C_5 fractions, may be used for further processing at a pressure of 5 atm. There are no technical problems that would prevent implementation of the new unit in industry at the present time. Figures 7, tables 4; references 8: 5 Russian, 3 Western.

A Study of the Acidity of Cracking Catalysts That Have Been Modified by Tin Compounds

[Article by E.A. Karakhanov, S.V. Kardashev, and S.V. Lysenko, Moscow State University imeni M.V. Lomonosov]

[Abstract] In an effort to reduce cracking catalysts' susceptibility to contamination by such metals as nickel and vanadium, the authors of the study reported herein examined the interconnection between a catalyst's activity and acidity and the implications of this interconnection with respect to protecting cracking catalysts against vanadium contamination. To measure the activity of specimen cracking catalysts, the authors subjected vacuum gas oil (of a mixture of Western Siberian and Tatar oils with boiloff points of 300 to 500°C) to cracking at a temperature of 500°C. The commercial zeolite-containing catalyst KMTs-UB (specific surface, 190 m²/g) was used. The acidity of the specimens was

determined by the method of thermal desorption of ammonia. The specimens were saturated with ammonia in an isothermal mode at 100°C, and the temperature was gradually raised to 600°C at 100°C increments. Each catalyst was impregnated with a solution of vanadyl naphthenate and with stannous chloride of C_7-C_9 fatty acid fractions in hexane such that the vanadium content amounted to 0.37 mass percent and the content of modifiers ranged from 0.15 to 0.35 mass percent. All of the catalysts were dried at 150°C and roasted at 630°C in an air current. The specimens' activity and acidity were then determined. The studies revealed that vanadium contamination does indeed reduce a cracking catalyst's activity. This reduction in activity is expressed in terms of a drop in conversion by about 8 mass percent, a drop in the gasoline yield by about 8 mass percent, and an increase in the yield of undesirable hydrogen product by about 0.17 mass percent and undesirable coke product by 1.6 mass percent. This reduction in catalytic activity was linked mainly to the destruction of the zeolite's crystalline structure. The formation of the desired end products of cracking, i.e., gasoline and light gas oil, was found to primarily involve the medium-acidity acid centers. Formation of the undesirable by-products (coke and hydrogen) was found to occur on high-acidity catalytic centers. It was discovered that treating the specimens with optimal amounts of stannous modifier (0.15 to 0.3 mass percent calculated for Sn) results in an acid center distribution close to that of fresh catalyst and results in a significant increase in the gasoline yield (2-3 mass percent) and conversion (by about 2.5 mass percent), as well as a reduction in undesirable coke and hydrogen by-products. Adding larger amounts of modifiers (i.e., in amounts greater than 0.3 mass percent) led to a reduction in the fraction of medium-acidity centers and all the negative consequences thereof. Figure 1, table 1; references 5: 2 Russian, 3 Western.

Hydrogenation of Aromatic Nitro Compounds on Soluble Metal-Polymer Catalysts

[Article by E.A. Karakhanov, M.V. Klyuyev, L.V. Ter-eshko, O.V. Kalinina, and A.G. Dedov, Moscow State University and Ivanovo State University]

UDC 541.128

[Abstract] The authors of the study reported herein studied the hydrogenation of a number of nitro compounds in the presence of catalysts based on palladium or rhodium and polyacrylic acid [Pd-PAA and Rh-PAA]. The hydrogenation was conducted under soft conditions (temperature, 20 to 60°C; p_{H2}, 0.1 MPa. Aromatic amines were observed to form in the case of the Pd-containing catalysts, whereas alicyclic amines formed in the case of the Rh-containing catalysts. The hydrogenation of dinitrobenzenes on Pd-containing catalysts was observed to entail the intermediate formation of nitroanilines, whereas phenylenediamines formed immediately on the rhodium-containing catalysts. After studying the kinetics of the hydrogenation of aromatic nitro compounds, the authors proposed a two-stage hydrogenation mechanism. In the first stage, the molecules of the nitro compound interact with the catalyst's active centers, resulting in the formation of adducts. (These adducts evidently form because of the partial transfer of the electron density between the d-orbitals of the palladium and the π-electron system of the benzene ring or nitrogen-oxygen bonds of the nitro compound.) In the second stage, the adducts react with the hydrogen, resulting in the appearance of hydrogenation products in the reaction mixture. After analyzing the kinetic parameters of the hydrogenation of nitrobenzene on selected palladium catalysts, the authors noted a significant reduction in effective activation energy upon the transition from palladium black or Pd/C to palladium-containing polymers. Figures 5, tables 2; references 5: 3 Russian, 2 Western.

Catalytic Oxidation of Unsaturated Aldehydes by Hydrogen Peroxide

[Article by Z.G. Pikh, N.I. Kosmina, V.Ya. Samarik, and A.A. Sheredko, Lvov Polytechnic Institute]

UDC 547.38;546.215

[Abstract] The authors of the study reported herein examined the reaction of unsaturated aldehydes (acrolein, methacrolein, ethylacrolein, crotonaldehyde, and 2-ethylhexene-2-al) with hydrogen peroxide in the presence of various catalysts. As catalysts, the authors used Se, Mo, W, Ce, and Te compounds (which form peroxy acids when held in concentrated H_2O_2). The reaction of unsaturated aldehydes with hydrogen peroxide was found to proceed most rapidly in the presence of Se compounds. The said reaction occurred with a high selectivity (92 to 94%) with respect to the formation of unsaturated acid. In view of the toxicity of Se, however, the authors continued their search for other catalysts. Further studies revealed that using other catalysts results in the formation of a complex mix of by-products. A strong connection between the structure of the aldehyde and reaction products was noted. This connection is discussed in some detail, and a diagram of the proposed mechanism of the formation of the reaction products and the kinetics of their accumulation is presented. The said mechanism may be summarized as follows: Upon interaction with hydrogen peroxide, the catalyst forms a peroxy form catalyst that in turn reacts with the unsaturated aldehyde in two directions. The first direction entails the implantation of oxygen at the C-C bond, which results in the formation of a formate that, upon

hydrolysis, yields methyl ethyl ketone. The second direction entails the formation of an unsaturated acid that is then hydroxylated to glycol by hydrogen peroxide. The glycol then oxidizes to ketonic acid and formic acid. The studies reveal that the rate at which hydrogen peroxide is consumed in its reaction with unsaturated aldehydes is very much dependent on the solvent and catalyst used. The most active compounds in the said reaction are Mo, Ce, and W. The structure of the oxidized aldehyde also exerts a strong effect on the reaction speed. From the standpoint of oxidation speed, the aldehydes studied may be ranked as follows: crotonaldehyde > 2-ethylhexene-2-al > acrolein > methacrolein > ethylacrolein. Figures 5, table 1; references 7 (Russian).

The Oxidative Conversion of Propane Into C_2-C_3 Olefins on Manganese-Containing Catalysts in the Presence of HCl

[Article by A.Kh. Mamedov, S.R. Mirzabekova, S.A. Dzhamalova, and V.S. Aliyev, Petrochemical Processes Institute, Azerbaijan Academy of Sciences]

UDC 547.213:542.941.8

[Abstract] The authors of this article conducted a study to determine the laws governing the oxidative conversion of propane into C_2-C_3 olefins on manganese-containing catalysts in the presence of HCl. Their goal in so doing was to clarify the effect that the nature of the starting hydrocarbon has on the mechanism of activation of the C-H bond in the presence of HCl. The experiments were conducted in a flowthrough system in a vibration-rarefied catalyst layer in the temperature interval from 600 to 800°C. A propane-and-air mixture containing 8 to 15 volume percent C_3H_8 was used as a starting material. Two catalysts were used: (1) Na-Mn/SiO_2 produced by impregnating silica gel with manganese nitrate and caustic soda solutions (Na content, 8%; Mn content, 17%) and (2) the same catalyst but processed with a reaction mixture of air + 1% HCl at 750°C for 1.5 hours. Four cubic centimeters of catalyst was used in a catalyst layer 7 cm deep. The crystalline structure of the Na-Mn catalyst and its phase transformations were studied in situ with a DRON-2.0 x-ray diffractometer with FeK_α radiation. The reaction mixture was fed at a rate of 8 cm^3/min; the catalyst weighed 1.05 g. In the absence of a catalyst, propane conversion at temperatures below 700°C is generally low, i.e., it does not exceed 50%. Adding 1% HCl to the reaction mixture was found to increase propane conversion to 60.2%. The total selectivity with respect to C_2-C_3 olefins increased only slightly, however. It also remained unchanged when the temperature was increased from 700 to 750°C. This was true regardless of whether HCl was present in the

reaction mixture or not. The increase in propane conversion in the presence of HCl was attributed to the participation of chlorine in the homogeneous activation of propane and the occurrence of a four-step initiated decomposition process detailed in the article. Experiments on the transformation of propane on the first of the aforesaid catalysts demonstrated the formation of ethylene and products of its deep oxidation. When this catalyst was used, selectivity with respect to C_2H_4 increased with temperature. Using the second of the aforesaid catalysts produced analogous results: Propane conversion increased significantly when HCl was added to the reaction mixture, both at low and high propane temperatures. The absence of an oxide phase in the system NaCl·$MnCl_2$ led the authors to conclude that the process of the oxidative conversion of C_3H_8 in the presence of HCl occurs exclusively via the chloride route. The propane transformation mechanism proposed herein is said to differ greatly from the mechanism of the oxidative conversion of methane and ethane. These differences are discussed briefly. Figures 2, tables 3; references 10: 9 Russian, 1 Western.

The Physicochemical and Heat Engineering Properties of Coals of the Apsatsk Deposit

[Article by N.V. Novitskiy, N.P. Kochkina, O.A. Filippova, and A.V. Bannikova, Ural affiliate, All-Union Heat Engineering Institute imeni F.E. Dzerzhinskiy]

UDC 662.66.001.5

[Abstract] The authors of the study reported herein examined the physicochemical and heat engineering properties of coals from the oxidation zone of sections of the Eastern and No. 2 Central Apsatsk deposit (in the Baykal-Amur area). The coal found in the No. 2 Central section is brown coal (primarily type Zh), and that found in the Eastern section is type K brown coal. A total of 29 differential-stratal specimens and enclosing rock from the two sections were studied. The coals' average quality indicators were established along with dependences between the quality indicators (30 in all) that can be used under practical conditions. For example, they develop a dependence linking maximum moisture capacity and hygroscopic water content and discuss the dependence of density and ash content and the dependence of slag formation temperature on ash composition. The maximum moisture capacity of the coal specimens taken from the No. 2 Central section was found to lie in two ranges depending on depth: Specimens from a depth of 27.9 to 31.9 m were found to have a maximum water content (W_{max}) of 4.1 to 4.8%; for specimens taken at a depth of 66.2 to 79.0 m, W_{max} = 2.0 to 2.7%. The presence of agrillaceous minerals of the montmorillonite group in the inorganic part of the coal from the No. 2 Central section was demonstrated. Because of this fact,

the said coals did not manifest the relationship between W_{max} and ash content (A^d) (i.e., a decrease in W_{max} as A^d increases) that is characteristic of most of the country's power generating coals. The coal taken from the Eastern section was found to have an SiO_2/Al_2O_2 ratio between 1.42 and 2.49, which indicated that its inorganic portion contains agrillaceous minerals of the kaolinite and illite group. The ash content of the coals from the No. 2 Central section, on the other hand, was between 2.7 and 3.57. The slag formation and fouling properties of the said coals' ash were determined in accordance with the slag formation (R_s) and fouling (R_f) indicators proposed by the firm Babcock and Wilcox. In the case of the specimens from the Eastern section, $R_s = 0.09$ and $R_f = 0.43$; in the case of the coals from the Central No. 2 section, $R_s = 0.2$ and $R_f = 0.61$. The authors conclude that the coals studied may be used successfully at thermal electric power plants provided that consideration is given to the characteristic features of the coals' makeup and properties. Figure 1, table 1; references 19: 17 Russian, 2 Western.

Helium Sorption by Mined Coals

[Article by N.F. Batrakov and E.A. Bineyev, Novocherkassk Reclamation Engineering Institute]

UDC 622.02

[Abstract] The authors of the study reported herein proposed a new method of studying the sorption of helium and other gases that are not sorbed in high amounts by mined coals. Specifically, they propose a new method of measuring the free volume of sorption ampules based on helium input-output. The new method does three important things: (1) it increases the reliability and precision of measuring helium sorption, (2) it provides a definitive confirmation that helium is indeed sorbed by naturally moist coal, and (3) it makes it possible to determine the quantity of helium or any other little-sorbed gas that has been sorbed. The measurements taken by the authors of the volume of a coal-filled ampule as the coal dries out confirm that despite prevailing ideas, the free volume of the sorption ampule does not increase. The helium does not penetrate into that space of the coal that was previously occupied by water. This raises doubt regarding the validity of making corrections for the volume of water in naturally moist coal. After experimentally establishing the fact that helium is indeed sorbed by naturally moist coal, the authors hypothesize that it is the hydroxyl groups of the hydrated surface of moist coal that are the main sorption centers of the helium molecules. Figures 2, table 1; references 6: 5 Russian, 1 Western.

The Correlation Between the Physiological Activity and Physicochemical Properties of Humic Preparations

[Article by S.G. Gagarin, L.N. Yekaterinina, and R.Kh. Alyautdinova, Mineral Fuels Institute]

UDC 662.743

[Abstract] The use of brown and oxidized brown coals to produce humic fertilizers and plant growth stimulators is a promising direction in coal chemistry. As phenolcarbolinic acids containing various functional groups, humic acids have a multifaceted effect on plant growth. In view of these facts, the authors of the study reported herein examined the effect that thed method used to isolate humic acids from brown coal has on the yield, makeup, and properties of the humic acids. They also sought to establish quantitative dependences between physiological activity indicators and the characteristics of the makeup and structure of humic acid preparations. For their studies, the authors used brown coals with an ash content not exceeding 4.5%. The following methods of extracting humic acids were tested: one-time alkaline extraction, gradual alkaline extraction, vibratory grinding in different media, and the use of low-frequency vibration effects. As a control, the authors isolated total humic acids by the pyrophosphate method in accordance with All-Union State Standard [GOST] 9517-76. A comparison of humates dried under soft conditions (40°C in a vacuum) and more stringent conditions (100°C on a drying rack) revealed that the latter exhibit somewhat of a reduced physiological activity. The results of tests performed on 19 specimens of extracted humic acids were subjected to correlation and multifactoral regression analyses. The results were presented for use in optimizing processes to extract humic acids from brown coals. The Zhilevo OPOF [not further identified] has recently installed and begun operating a unit to produce sodium humates by the method of one-time alkaline extraction. Their stimulant effect has been confirmed by a physiological activity study, and field tests have demonstrated that they increase crop yields an average of 15 to 25%. Figure 1, table 1; references: Russian, Western.

The Oxidation of Carbonaceous Substances in the Presence of Alkaline Metal Hydroxides

[Article by Ye.S. Rudakov, L.P. Metlova, V.S. Chuprina, and V.A. Sapunov, Physical Organic Chemistry and Coal Chemistry Institute, UkSSR Academy of Sciences]

UDC 543.226:66.094.37:546.26

[Abstract] The authors of the study reported herein conducted a study to obtain systematic data regarding the catalytic effect of hydroxides and salts of alkaline metals on the oxidation of a number of carbonaceous substances, including graphites, carbon black, glassy carbon, pitch coke, anthracites, and activated charcoal. Specifically, the following carbonaceous substances were studied: GT-1 crucible graphite; spectroscopically pure pyrolysis graphite; pseudo-monocrystalline graphite; glassy carbon (processing temperature, 2,000°C); pitch coke; expanded fine-crystalline graphite produced from GT-1 graphite; A1 Donets anthracite; A4 Donets anthracite; low-activity coke carbon (P-803 carbon black); low-temperature coke produced from carbon deposits on a zeolite methanol conversion catalyst; polyacrylonitrile [PAN] carbon fiber heat-treated at 1,400°C; and type-BAU activated charcoal. The following are among the key study findings: The temperature of the maximum rate of mass loss during the catalytic oxidation (in the presence of KOH) of the graphites, activated charcoal, PAN fiber, carbon black, coke, and glass carbon is lower than that in the case of noncatalytic oxidation. The temperature shift increases as the KOH concentration is increased: When 1 mol/kg is applied, the change ranges from 25 to 300°C depending on the nature of the given carbonaceous substance. Under noncatalytic conditions, the differential thermogravimetric analysis [DTG] curves for the coke deposits on zeolite catalysts exhibit a peak with an arm that is split into two peaks when KOH is present. The catalytic effects observed increase in the following series $Li^+ < Na^+ < K^+ < Cs^+ < Rb^+$ and $Cl^- < Br^- < CO_3^{-2} < OH^-$. The authors propose a quantitative method of analyzing the content of two forms of coke in carbon deposits on catalysts. Figures 3, tables 2; references 11: 4 Russian, 7 Western.

Hydrogenation of Coals From the Kangalassy Deposit in the Presence of an Fe-Mo Catalyst

[Article by N.I. Artemova, A.P. Yegorov, D.V. Kler, L.I. Kasatochkina, and V.R. Chizhevskaya, Mineral Fuels Institute]

UDC 62.73:519.272

[Abstract] The authors of the study reported herein examined the material makeup and chemical properties of coals from the Kangalassy deposit. They subjected specimens of the said coals to technical, elemental, functional, and petrographic analyses. They also studied the coals' reactivity during hydrogenation. Ten samples from different strata and two core samples from two boreholes were subjected to petrographic analysis, as were five trench samples from the upper and lower seams and one process sample from that section of the deposit that is being actively worked. The coal samples were subjected to hydrogenation in an autoclave (all of the samples were hydrogenated in a 0.5-l autoclave except for the sample from the process sample, which was hydrogenated in a 0.2-l autoclave). An Fe-Mo catalyst was applied to the dry coal by impregnation with solutions of Fe and Mo salts. Comparative analysis of data on five of the study specimens revealed significant differences in their degree of transformation as a result of hydrogenation. The findings for samples from the central portion of the upper and lower seams and the process sample were similar: degree of transformation of the coal's organic matter, 70.0 to 73.0%; yield of liquid products, 67.5 to 70.7%; and yield of gaseous products, 17.2 to 20.5%. The specimens taken from the two boreholes were characterized by a lower degree of transformation of the coal's organic matter (58.5 to 58.7%). The output of liquid products remained close to that of the other specimens, however (i.e., 67 to 70%). Because the said coal samples did not demonstrate adequate transformation into liquid products upon hydrogenation in the presence of an Fe-Mo catalyst, the authors decided that the use of an emulsified Mo-S catalyst would be required to achieve a high degree of transformation of the study coal into liquid products. Using the Mo-S catalyst increased the degree of transformation of the coals' organic matter to 86.0%, increased the yield of liquid products to 87.5%, and reduced the yield of gaseous products to 7.7%. Tables 4; references 7 (Russian).

Thermal and Thermochemical Destruction of Oil Shales

[Article by Kh.E. Luyk, I.F. Blyakhina, Chemistry Institute, Estonian Academy of Sciences]

UDC 662.67.66.060

[Abstract] The authors of the study reported herein worked to develop an efficient process for producing a liquid product from various oil shale. They then turned their attention to the characteristic features of the chemical reaction of the kerogen of these products with the following reagents: CO_2, HN_3, $(NH_4)_2CO_3$, $(NH_2)_2CO$, $HCOONa$, zinc dust, ethanol, isopropanol, and aqueous mixtures of the aforesaid. To obtain fairly stable structural fragments of the kerogen of the study shales, the researchers used a destruction temperature of about 100°C below the shales' dry distillation temperature. A two-stage kerogen destruction method was used to study the kerogen's structure. In essence, the method called for autoclave rarefaction in a medium of low-boiling solvents (including benzene and CO_2) followed by pyrolysis of the heavy (primary) fractions isolated from the total extract. This approach made it possible to conduct comprehensive studies of the kerogens of the various oil shales as well as their individual primary and secondary

products. The studies performed confirmed that using vapor- and gas-phase solvents to rarefy shale kerogen results in a high yield of high-viscosity liquid product. The amount of asphaltenes in this product is highly dependent on the process conditions (temperature and process duration). The maximum yield of liquid product corresponds to the maximum asphaltene yield. When oil shales are rarefied in a medium of CO_2, benzene, water, and C_2-C_3 alcohols, the yield of liquid product increases linearly with both the temperature and duration of rarefaction in the respective ranges from 300 to 380°C and 1 to 8 hours. The amount of gas formed is less than 5% of the kerogen. Detailed data were obtained regarding the output and characteristics of the rarefaction products of shale from the Dzhamsk deposit (process time, 4 hours; process temperature, 360°C). These data are compared with corresponding data for the rarefaction products of kukersite (Kukhruze oil shale). By using the aforesaid two-state rarefaction and pyrolysis method, the authors were able to obtain detailed information regarding the sequence in which the decomposition products are formed and to obtain new data on the little-studied asphaltenes and high-polar malthene fractions formed. Gas chromatography studies of the volatile pyrolysis products revealed that the secondary pyrolysis products contain fewer ketones but significantly more aromatic compounds than do the primary malthenes. The secondary malthenes also contain a notable amount of 1-olefins. Figures 3, table 1; references 6: 3 Russian, 3 Western.

The Reaction of Viscose Carbon Fibers With Coal-Tar Pitch During Heat Treatment

[Article by V.Ya. Posylnyy, V.V. Vitkovskiy, Yu.M. Lebedev, A.M. Bezuglov, and V.M. Belenchenko, Shakhtinsk affiliate, Novocherkassk Polytechnic Institute, RSFSR Ministry of Education]

UDC 662.74:546.26

[Abstract] The authors of this concise report studied the behavior of a mesophase of medium-temperature coal-tar pitch at the surface of various heat-treated viscose carbon fibers. As a starting product, the authors used viscose fiber that had been partially carbonized in a reducing medium (280°C). Specimens of the fiber were carbonized in the presence of helium to 400, 530, 600, 700, and 950°C. Commercial graphitized (temperature, 2,400°C) viscose carbon fibers made of the same starting material were also used. Two samples of each of the above specimens were used. One sample in each pair was impregnated with pitch and heated to 1,250°C in an anthracite booster; the other was placed in a thermostatted test tube with a melt of fresh pitch and held for 6 to 10 hours at about 400°C. Polished sections of each were subjected to microstructural studies. The studies

revealed that the growth of a mesophase in the study composites may occur in the directions to and from the carbon fibers' surface. Heating treating carbons fibers with an identical starting composition at different temperatures resulted in the adhesive strength of the contact between the said fibers and a coke binder. A correlation was discovered between the adhesive strength of the contact between viscose carbon fiber and coal-tar pitch that had been subjected to medium-temperature heat treatment and the activation energy of the carbon fiber's conduction of direct current. References 2 (Russian).

The Structure of Carbon Fibers Based on X-Ray Photoelectron Spectroscopy Data

[Article by F.F. Kugeyev, Ye.M. Baytinger, Yu.A. Teterin, and S.G. Gagarin, Chelyabinsk Pedagogical Institute]

UDC 546.26-162

[Abstract] The authors of this article used the method of x-ray photoelectron spectroscopy to examine the valence band of carbon fibers. X-ray photoelectron spectra of the study fibers were obtained on an HP 5950 x-ray photoelectron spectrometer in a vacuum of 10^{-7} Pa at room temperature using monochromatized radiation. The natural surface of specimens of polyacrylonitrile fiber laid in a single layer was used in all tests performed. Specimens of the said fibers were subjected to heat treatment over a broad temperature range (1,400 to 3,100°C) in an induction furnace. The specimens were held in an inert medium at the maximum temperature for 5 minutes. Heat treatment was found to change the shape of the spectra. The most significant changes were observed at bond energies of 10 to 10 eV, i.e., near the bottom of the valence band. Only two peaks, at 10.5 and 14 eV, dominated in the spectrum of the starting fiber. Heat treatment resulted in the splitting of one of these peaks and in the isolation of an additional maximum. In the spectrum of the specimen heated to 3,100°C, it was well resolved at a bond energy of 17 eV. Somewhat of a decrease in the intensity of the maxima of the spectra was also observed at low bond energies. The data obtained confirmed that the process of the formation of a coaxial carbon skeleton resulting from thermochemical transformation of the polyacrylonitrile into carbon fiber is not a monotonic process. The role that the transition associated with the change in the coordination circle plays in this process was investigated. The studies performed indicated that the carbon polyacrylonitrile fibers studied have a two-phase structure that contains both a graphite-like component and a chain component. When they are subjected to heat treatment, the fibers undergo interphase transformations facilitating graphitization of the end product. Figures 3; references 10: 8 Russian, 2 Western.

Changes in the Properties of Vermicular Graphite Upon the Implantation of CO_2

[Article by V.V. Shapranov, A.P. Yaroshenko, V.A.
Kucherenko, and I.V. Zverev, Physical and Organic
Chemistry and Petrochemistry Institute, UkSSR
Academy of Sciences]

UDC 546.26-163:66.083:546.264-31

[Abstract] Vermicular graphite is a layered compound
resulting from the implantation of sulfuric acid in
graphite encapsulated in a shell of magnesium salts.
Vermicular graphite is capable of increasing its apparent
volume upon heating, which is why it may be used in
exothermal antishrinkage mixtures in steelmaking. It is
also useful in extinguishing burning sodium in nuclear
power plant accidents and in producing foam graphite
(the main component in current-conducting adhesives).
In view of the importance of vermicular graphite, the
authors of the study reported herein examined the
changes in its properties resulting from implantation of
CO_2. They studied the short-term (10 to 60 minutes)
effect of carbon dioxide at an elevated (4 MPa or more)
pressure in the stages of the production of vermicular
graphite or, as it is also called, graphite bisulfate (C^+_{96-}
$_{120}HSO_4^- \cdot 2.5H_2SO_4$). To produce the vermicular
graphite, the authors used a three-stage process simu-
lating the commercial technology: The graphite powder
was treated in an aqueous solution (50%) of chromium
trioxide for 10 minutes. It was then treated with sulfuric
acid (94%) for 15 minutes. The excess H_2SO_4 was
neutralized by magnesium oxide (the vermicular
graphite particles were encapsulated in magnesium
salts). The best product was obtained when GT-1
graphite and 0.42 moles of CrO_3 per kilogram of graphite
and 3.7 moles of H_2SO_4 per kilogram of graphite were
used. Studies performed on the resultant compound
revealed that, when heated, it can swell by a factor of 1.5
to 4.0. Contact with Ar, N_2, He, and $N_2 + O_2$ (at a
pressure of 12 MPa or less) did not change the vermic-
ular graphite's properties. This was explained by the
formation of a stable bisulfatebicarbonate layered
graphite compound at elevated pressures. Figures 3,
table 1; references 19: 6 Russian, 13 Western.

Synthesis and Morphology of Particles of Microflake Graphite

[Article by A.V. Melezhik, L.V. Makarova, M.M.
Konoplya, and A.A. Chuyko, Surface Chemistry Insti-
tute, UkSSR Academy of Sciences]

UDC 661.666.2:541.18.053+541.18.058+541.182.021

[Abstract] Disperse graphite materials are widely used in
engineering. The authors of this article synthesize a type
of disperse graphite consisting of microflakes on the
order of 10 to 100 μm and ranging in thickness from n x
10^{-2} to n x 10^{-1} μm. The fractional makeup of the new
microflake graphite was determined by sedimentation
and photometry studies. Specimens of the new
microflake graphite were found to be characterized by an
effective sedimentation radius of 3 to 6 μm and a
weighted-mean form factor (ratio of flake length to
thickness) of 240. Some of the flakes and fragments of
the larger flakes were semitransparent in visible light.
The finely dispersed fractions, which are present in small
amounts, were found to be characterized by lower form
factors than the main fraction was. In principle, the new
microflake graphite's form factor is high enough to
achieve a reinforcing effect. The flakes' nonuniform
thickness and ragged shape in a plane may, however,
reduce their promise as a filler material. The authors
conclude that the new microflake graphite synthesis
technique appears to be a promising alternative to the
currently existing methods of producing graphite
microflakes and graphite films, which are rather compli-
cated and expensive. Figures 4; references 19: 14 Rus-
sian, 5 Western.

The Possibility of Using Geothermal Methods To Predict the Location of Hydrocarbons

[Article by A.I. Fialko, V.I. Oleksyuk, and L.V.
Dubitskaya, Kiev State University and Ukrgazprom
Production Association]

UDC 550.836(477.9)

[Abstract] Most of the petroleum and gas deposits
located in the Dneprovsk-Donets Basin have already
been worked to a depth of 3,000 to 4,000 m. Holes to
find new deposits are now being drilled to depths of
5,000 m or more. Geophysical prospecting methods are
thus becoming increasing important in the area. In view
of this fact, the authors of this article have proposed a
new method of predicting the depth at which hydro-
carbon deposits are located. The new method is based on
estimating the degree of nonlinearity of the geothermo-
gram of a borehole near that regional impervious bed
over a deposit that is closest to the surface. In developing
their method, the authors make use of the concepts of the
radius of curvature of the geothermogram and its rela-
tionship to the rate of the vertical filtration of fluid
through the rock (i.e., the Knudsen number): The value
found for the Knudsen number is determined to be
directly proportional to the volumetric porosity of the
rock and inversely proportional to the radius of curva-
ture of the geothermogram and the temperature gra-
dient. The new method was used to estimate the gas

content of the deep zone of the Shebelinsk deposit (the largest natural gas deposit in the Ukraine). The new method was used to estimate the deposit's gas content at a depth of 600-800 m. The estimate was in agreement with existing data. The method was then used at a depth of 2,300 to 2,500 m (below the deposit's gas-water contact). The results obtained accounted for the anomalously low productivity of boreholes that had previously been drilled in the central portion of the deposit and indicated sites that appear more promising for drilling. The prospective sites likely hold younger deposits with lithologic or tectonic traps ascribed to fault zones. The authors recommend a trial of their proposed method throughout the entire Dneprovsk-Donets Basin territory so as to (1) confirm its feasibility on a yet broader scale by comparing the data obtained with existing data and (2) obtain a better idea of the prospects of those areas of the deposit that have not yet been reached by drilling. Figures 3; references 5: 4 Russian, 1 Western.

Prospective Oil and Gas Contents of the Mid-Carboniferous Period Deposits of the Southeastern Portion of the Dneprovsk-Donets Basin

[Article by R.M. Novosiletskiy (deceased) and Ye.M. Prikhodko, Ukrainian Mining Scientific Research Institute]

UDC 553.981.552.1:53(477.6)

[Abstract] The authors of this article take a new look at the prospective oil and gas content of the mid-Carboniferous deposits of the southeastern portion of the Dneprovsk-Donets Basin. They base their assessment on the degree of lithification of gravel. Specifically, they conclude that the filtration-capacity parameters of the gravel collectors of productive levels have a porosity ranging from 2-4 to 25-30% and a permeability ranging from 0.1 x 10^{-3} to 800 x 10^{-3} μm^2. Detailed maps of (1) the depth of propagation of gravel collectors and (2) the maximal porosities of gravels of the mid-Carboniferous deposits of the southeastern portion of the Dneprovsk-Donets Basin. The authors conclude that the geological structure of the southeastern portion of the basin facilitates the formation of hydrocarbon deposits in the form of migration flows in the direction of the areas near the basin's sides and onward to the points at which the fluids are released. Similar hydrocarbon deposits are known to exist in a number of oil-and-gas-bearing basins in the Ukraine in the Carpathian depression. Fluids in the form of migration streams of hydrocarbon gas are released along those rocks with an elevated porosity and permeability that were transformed in the stage of early catagenesis. Those structures in the cross section of the Mikhaylovskoye, Kremenovkoye, Novoselovskoye, Proletarskoye, and Leventsovskoye deposits in the southern

side area and the Yulevskoye, Shevchenkovskoye, and Druzhelyubovskoye deposits in the north are deemed especially attention worthy. The following structures are said to be promising from the standpoint of searching for hydrocarbon deposits: Vostochno-Razumovskaya, Doroshevskaya, Oktyabrskaya, Mazharovskaya, Shandrovskaya, Svetlanovskaya, Krasnooskolsyaka, Morozovskaya, Morozovskaya, Taranushinskaya, Kolomankskaya, and Kisovskaya. Figures 3; references 4 (Russian).

The Feasibility of Processing Regional OGT Profiles

[Article by R.V. Gerasimovich, VUGRE [not further identified]]

UDC 550.834.04

[Abstract] The author of the study reported herein discusses the results of the integrated processing of materials from regional and local OGT [not further identified] seismic studies conducted in the Kochubeyevsko-Chutovskaya area of the central portion of the Dneprovsk-Donets Basin. A new model of the area's geological structure is proposed that makes the area appear more promising as a site of gas-and-oil-bearing deposits. Specifically, the analysis performed led the author to conclude that the Voinovskaya and Chutovskaya structures are elements of a single anticlinal fold that developed at the southeastern end of the Solokhovsko-Dikanskiy bank. The formation of this site during the Carboniferous period was accompanied by the formation of faults along the bank's periphery. The industrial hydrocarbon reserves located within the bounds of the Chutovskaya structure are linked to Carboniferous and Lower Permian periods. Proceeding from the assumption that the Voinovskaya and Chutovskaya structures are both elements of the same anticlinal fold, the author then hypothesizes that the traps in the Chutovskaya area are also part of a natural reservoir formed within the bounds of a single paleo-Voinovskaya anticline. This fact makes the Voinovskaya structure as promising a site of hydrocarbon deposits as the Chutovskaya structure is. Figures 2.

Models of the Formation of Anomalously High Seam Pressures—A Basis for Predicting Seam Pressures

[Article by V.I. Voronin, Ukrainian Gas Scientific Research Institute]

UDC 622.279.031; 532.11:62

[Abstract] After analyzing a large number of domestic
and foreign literature sources, the authors of the study
reported herein conclude that all of the existing hypoth-
eses (a gradient of 0.0127 MPa/m or 0.130 kgf/(cm^2 x m)
or higher) regarding the formation of anomalously high
seam pressures [AHSP] may be reduced to two models.
The first is termed the evolutionary model, and the
second is termed the pulsation model. In both cases, the
main condition of the existence of AHSPs is the isolation
of accumulations of fluids: The more isolated these
accumulations are, the more likely it is that AHSPs will
occur. In the case of the evolutionary model, the fluids in
masses of terrigenous sedimentary rock with initially
normal seam and rock pressures are redistributed under
the effect of such evolutionary processes as packing and
dehydration. Fluids migrate from isolator-rock to collec-
tor-rock. The driving force behind this process is the fact
that the rock pressure increases at a faster rate than the
seam pressure does. If a collector is not isolated, the
pressure is "reduced" by moving through it and into the
isolator-rock. More interesting from the standpoint of
the formation of AHSPs is the case where the collector is
isolated on all sides and where the seam pressure in it
increases as the pore pressure in the surrounding fluid
trap-rock increases. Rather than acting as a screen, these
surrounding fluid traps perform serve as a source of
increased seam pressure. In this case, the anomalously
high rock pressure [AHRP] is primary, and the AHSP is
secondary. This fact is very important from the stand-
point of predicting AHSPs. Collector seams with AHSPs
are always surrounded by a halo of AHRP, but AHRP
does not always necessarily signal AHSPs. This factor
also affects attempts to predict AHSP. According to the
pulsation model, AHSP may form at any site where the
rate at which fluid pressure increases exceeds the rate at
which that same pressure relaxes. This phenomenon
occurs when the pulsation of fluid throughout permeable
regions is accompanied by the accumulation of the said
fluid. Such conditions arise in areas of intersection with
zones of fluid traps or deposits between and under salt
formations. In such cases the fluid traps act as caps and
thus play a passive role. The AHSP is primary, and
AHRP is secondary; consequently, the latter may not
exceed the former. The halo of AHRP associated with
this mode is typically much smaller than are the deposits
of fluids with AHSPs around which they form. The
evolution and pulsation models are discussed from the
standpoint of their use in predicting AHSPs during the
process of drilling boreholes. When the evolutionary
model is at work, the best methods to use are those that
are based on unequivocal information and that make it
possible to obtain a quick quantitative estimate of the
magnitude of fluid pressure in the section being uncov-
ered (including the d-exponent method). In cases where
the pulsation model is at work, the mud and helium
logging methods are best. References 12: 11 Russian, 1
Western.

Improving the Central Flushing Setup of Three-Cone Drill Bits

[Article by N.A. Zhidovtsev, V.B. Marik, and I.M.
Gubareva, MING imeni I.M. Gubkin [not further iden-
tified] and IFING [not further identified]]

UDC 622.24.082.2

[Abstract] Three-cone drill bits with central flushing
circuits have become quite popular and account for
48.5% of all drill bits produced in the Soviet Union. In
an effort to improve three-cone drill bits with central
flushing, the authors of the study reported herein com-
pared different design versions of three-cone drill bits
with central flushing. In the first such drill bits, the
central flushing circuit is in the form of an opening
(regardless of whether it is a round, triangular, or three-
slit opening). Only about 20% of the total amount of
flushing fluid directly reaches the bottom of the hole
being drilled (the rest was reflected from the cones and
seeped into the space beyond the annual channel). A
conical packing with a central outlet hole was developed
in an effort to improve the flushing circuit. The new
circuit improved fluid passage and increased mechanical
drilling speed by 10-15%, but it did not solve the
problem of transverse flows of drilling fluid. In hopes of
further improving the central flushing circuit,
researchers at the MING imeni I.M. Gubkin worked
together with workers at the Drogobych Drill Plant to
develop a drill bit that has a central slit backing with
internal cylindrical and conical cavities with round out-
lets and lengthwise slits along the generatrix of the
conical section. The total area of the lengthwise cuts and
area of the central outlet hole of the hydraulic channel
were in a 1.1:1.3 ratio to one another. This new flushing
circuit was subjected to comparative tests along with
other flushing circuit designs. The criterion used to
compare the efficiency of the various central flushing
schemes tested was that of the maximum relative rate of
transverse flow along the radius of the hole bottom in the
direction from the center to the periphery. A full-scale
three-cone drill bit with replaceable central flushing
nodes 215.9 mm in diameter was used for the tests. The
new flushing circuit was subjected to commercial tests.
Mechanical drilling speed was improved by 30 to 40%,
and packing on the drill bit was decreased significantly.
Figures 2, table 1; references 4 (Russian).

Diagnosing the Quality of Drilling Fluids

[Article by L.I. Dopilko and G.V. Zagidullina, Tyumen
Drilling Operations Administration]

UDC 622.243.144.1

[Abstract] Previous research on drilling fluid quality has shown that drilling fluids that have proved to demonstrate unsatisfactory performance actually conform to drilling fluid requirements regulated by such generally accepted physicomechanical parameters as density, tentative viscosity, filtration index, thickness of the filtration skin, hydrogen index, static shear stress, sedimentation stability, and daily sedimentation. In an effort to improve methods of assessing drilling fluid quality, the authors of the study reported herein examined the role of various parameters characterizing the performance properties of drilling fluids. Specifically, they examined the following rheological criteria: nonlinearity index (which directly characterizes the content of colloid phase in the fluid), the effective viscosity at a shear rate of 100 s^{-1} (which characterizes the fluid's fluidity), asymptotic viscosity at a shear rate of 10^4 s^{-1} (which characterizes the quality with which the drilling fluid has been cleaned), plastic viscosity, dynamic shear stress, and plasticity coefficient (which characterizes the drilling fluid's endurance). Analytical dependences for use in calculating the specified rheological parameters were developed and are presented herein. The dependences were derived for use with a VSN-3 rotary viscosimeter, which is the Soviet Union's only domestically produced rotary viscosimeter. To enable the said calculations to be performed quickly, the authors constructed nomograms and developed a program for the Elektronika BZ-34, MK-61, and MK-52 microcalculators. They have also included a table for use in classifying the quality of a nonweighted drilling fluid as excellent, good, satisfactory, or unsatisfactory based on the its nonlinearity index, effective viscosity, asymptotic viscosity, and plasticity coefficient. The numerical values presented for the indicator nonlinearity index are as follows: excellent, < 0.40; good, 0.40-0.53; satisfactory, 0.54-0.70, and unsatisfactory, >0.70. The numerical values presented for effective viscosity are as follows (MPa x s): excellent, 24-66; good, 20-50; satisfactory, 16-36; and unsatisfactory, 11-30. The values presented for asymptotic viscosity are as follows (MPa x s): excellent, 1.0-3.5; good, 2.5-5.0; satisfactory, 4.0-8.0; and unsatisfactory, 6.0-16.0. The plasticity coefficient values are as follows ($x10^{-2}$, s^{-1}): excellent, >5.0; good, 3.0-5.0; satisfactory, 1.5-2.9; and unsatisfactory, <1.5. Figure 1; references 4 (Russian).

Ways of Increasing the Insulating Value of Grouting Mortars

[Article by V.Ye. Akhrimenko, G.I. Gagay, A.Ye. Gorlov, and Ye.M. Levin, VNIIKRneft [not further identified]]

UDC 622.245

[Abstract] The authors of the study reported herein examined the effect of various factors on the quality of lining wells. They demonstrate that the insulating value of grouting mortars is especially important. They assess the insulating value of grouting mortars based on the pressure gradient at which filtration of fluid in the structure of the grouting mortar is observed. They further demonstrate that the insulating value of a grouting mortar may be increased by adding polymers to it. The effects of the following three additives were compared: type TR polyvinyl alcohol; type V3222 Vinarol (Hechst, FRG); and a mixture of methyl cellulose, aminoformaldehyde resin, and antifoaming agent that has become known as a reagent for grouting mortars (KRTR-75). Grouting mortars with the additive KRTR-75 were found to have the maximum insulating value. The beneficial effect of the KRTR-75 was explained as follows. Molecules of aminoformaldehyde resins interact with methyl cellulose molecules on account of their hydrogen bonds. This keeps methyl cellulose from coagulating at temperatures up to 75°C. At temperatures above this point, the strength of the bonds is reduced, and the methyl cellulose coagulates from the mortars. The resin molecules adsorbed on the cement grains increase the dispersion of the cement particles. This in turn increases the number of contact interactions between the particles and results in more intensive structure formation. KRTR-75 is resist to the formation of cracks, and it reduces the amount of water released from grouting mortars. Consequently, it increases their insulating value without affecting their setting time. KRTR-75 was added to grouting mortars used successfully on a number of wells in the Samotlorskoye deposit. All of the wells on which the grouting mortar was used yielded oil with a low water content. Figure 1, table 1.

Drilling Fluid Compositions Based on Asbestos Cement Wastes

[Article by Ye.N. Ignatenko and L.N. Loktionova, IKKhKhV imeni A.V. Dumanskiy [not further identified], UkSSR Academy of Sciences]

UDC 661.148

[Abstract] In an effort to utilize asbestos cement wastes that have accumulated, the authors of the study reported herein examined the feasibility of using asbestos cement wastes from the construction industry as aggregating agents for drilling fluids. To test the feasibility of using asbestos cement wastes for the said purpose, they heated asbestos-clay suspensions for 4 hours at a temperature of 150°C and a pressure of 60 MPa. The suspensions maintained the required performance parameters at the

test temperature and were also found to possess well-expressed thixotropic properties. The tests thus confirmed that partially replacing bentonite with asbestos cement waste results in high-quality drilling suspensions, reduces clay phase consumption, and intensifies the process of thixotropic structure formation under conditions of high mineralization. The use of asbestos cement wastes was also shown to reduce the effect of colmation of the area near the working face and to preserve the collector properties of the seam in a close-to-natural state and thus improve the quality of uncovering productive levels. The authors further proposed that asbestos cement wastes used in drilling fluids be modified by GKZh-94 polyethyl hydroxide siloxane. The purpose of this modification is to increase the fluids' rheological properties, reduce their filtration, and increase their strengthening properties. Both the asbestos cement and GKZh-94 were found to possess a good resistance to heat destruction and thus increase the drilling fluid's heat stability. The new drilling fluid was introduced at the Turkmensevburgaz Drilling Operations Administration Production Association, where it resulted in an annual cost savings of 689,100 rubles. The authors thus succeeded in developing what they term a new ecologically pure asbestos-clay flushing fluid. Tables 3; references 4 (Russian).

Improving Methods of Estimating Economic Losses Based on Weather Conditions

[Article by A.V. Yashchenko, Ye.P. Uryuzhnikov, and V.A. Shokun, Sevastopol Department, State Oceanographic Institute and Chernomorneftegas Production Association]

UDC 551.5

[Abstract] The authors of this article propose a general methodological approach to estimating economic losses based on weather conditions during offshore recovery of oil and gas. The method is based on calculation of the bad weather coefficient. This coefficient makes it possible to give consideration to hydrometeorological conditions such as high wind speed and high waves that increase the costs of constructing and operating offshore drilling rigs. The bad weather coefficient is used to estimate weather-related increases in wages, the cost of operating machinery and equipment, and the cost of boats and floats. A formula for calculating the bad weather coefficient is provided. The following are taken into consideration when the coefficient is calculated: the total duration of the operations, that portion of the total working period during which hydrometeorological conditions are acceptable for offshore work, the hydrometeorological index, the duration of the hydrometeorological observations conducted to determine the hydrometeorological index, the number of working rigs subjected to the said hydrometeorological conditions, and the number of synoptic situations (as taken from synoptic map archives). Two methods are presented for estimating the amount of time that weather conditions do not prevent work. The accuracy of determining the bad weather coefficient is discussed. Special attention is given to the problems entailed in calculating the said coefficient at high sea. The matters of seasonal differentials in the bad weather coefficient and year-to-year weather variations are also discussed. The authors conclude that using the proposed approach to calculating the bad weather coefficient will increase the economic effectiveness of the estimated normalization of costs for the operations entailed in recovering oil and gas at sea and in conducting the said operations in optimal time periods. Figure 1; references 7 (Russian).

Calculating the Rate of the Hydroabrasive Wear of Jet Devices' Mixing Chambers

[Article by L.V. Gudziy, B.S. Dolishniy, and Yu.S. Zamora, Nedra Special Technological Design Office]

UDC 621.694

[Abstract] The authors of the study reported herein examined the problem of calculating the rate of hydroabrasive wear of the mixing chamber of a jet device. They perform their analysis for the case of the wear of the flowthrough portion of a mixing chamber that results from the cutting action of abrasive particles passing through the chamber and cutting into the plastic material of which it is made. Through a series of calculations the authors demonstrate that the rate at which a mixing chamber experiences hydroabrasive wear depends on the pressure differential and the diameter of the nozzle. The rate of hydroabrasive wear increases as the pressure differential and nozzle diameter increase. Figure 1.

Determining the Compressibility Coefficient of Sour Hydrocarbon Gases

[Article by B.V. Kichenko, S.G. Butkevich, and V.V. Maystrenko, YuzhNIIgiprogaz]

UDC 553.2

[Abstract] The authors of this article describe methods of determining the compressibility coefficient of hydrocarbon gases with a high content of acidic components (hydrogen sulfide and carbon dioxide) that are known and used abroad. They present a modification of the procedure that Standing and Katz developed to calculate

the compressibility coefficient of hydrocarbon gases containing less than 10% acid components by volume. The modification presented is intended for use in determining the compressibility coefficient of high-sulfur gas. The basic procedure is the same in both cases. The main difference is that the method used to calculate the compressibility coefficient of high-sulfur gases entails using a correction factor that was initially proposed by Wichert and Aziz. The authors detail a procedure for computer-assisted graphic-analytical and computational-analytical determination of the compressibility coefficient of the aforesaid hydrocarbon gases. They present a 15-step algorithm in which the molecular weight of the i-th component of the gas mixture and the relative density of the gas serve as source data. The authors state that the algorithm presented is especially promising for using in calculating the compressibility coefficient on a programmable microcalculator. Figures 3, table 1; references 7 (Western).

Intensifying Oil Refining at the Kherson Oil Refinery

[Article by A.P. Somikov, N.G. Litvinenko, A.I. Stekhun, and V.Ye. Klimenko, Kherson Oil Refinery and Bashkir Oil Refining Scientific Research Institute]

UDC 665.642.4

[Abstract] The authors of the study reported herein demonstrate the economic effectiveness of refining high-boiling oil fractions during the coking process at the Kherson Oil Refinery. They show that coking oil residues makes it possible to intensify oil refining and expand reserves of petroleum coke and medium-distillate fractions suitable for use in obtaining distillate fuels and effective water-repellent additives. Specifically, they examined the results of more intensive refining of the bitumen remaining after the refining of a commercial mixture of Western Siberian high-sulfur oil that has (at 20°C) a density of 988 kg/m^3, a cokability of 12.3%, and a coke-forming component content of 66%. When refined in a slow-coking unit, the said bitumen yields large amounts liquid (about 60%) and gaseous (10%) coke by-products. All of the coke distillates may be used to prepare two consumer products: A-76 gasoline for use in motor vehicles (as per All-Union State Standard [GOST] 2084-77) and light gas oil (the 180-350°C fraction) for use as furnace fuel (in accordance with specification TU 38.101656-87). The heavy gas oil obtained (the 350-485°C fraction) may be used to produce a water-repellent additive for wood boards conforming to GOST 4598-86 for water-repellent fiberboard. Tests have confirmed that the said water-repellent additive has a high penetrating ability that makes it possible to treat boards at a temperature of 60 to 70°C (as opposed to the temperature of 120°C required when tall oil is used). The new water-repellent additive also has better viscosity and temperature properties than tall oil does. A capital investment of about 190,000 rubles was required to set up production of the new water-repellent additive at the Kherson Oil Refinery. The new repellent can be produced at a cost of 45 rubles per ton and has a wholesale price of 65 rubles per ton. Producing 50,000 tons of the new water-repellent additive yearly will thus give the plant a yearly profit of 0.95 million rubles and will allow the plant to recoup its initial capital investments in less than one calendar quarter. Table 1; references 5 (Russian).

Stability of Polyisoprenes During Thermooxidation and Breakdown Plastification

[Article by S. V. Afanasyev, F. A. Nazarova, S. A. Lebedeva and V. V. Bogdanov]

UDC 678.762.3

[Abstract] A study of the effectiveness of protective action of antioxidants used during thermooxidation and breakdown plastification of SKI-3 and SKI-3-01 isoprene rubbers showed a similarity of SKI-3 and SKI-3-01 during thermooxidation and breakdown plastification in rubber mixing equipment. Unmodified polyisoprenes, especially SKI-3 stabilized by diaphene PP were the best of the filled vulcanizates. The lesser thermostability of rubbers based on SKI-3-01 than of those based on SKI-3 was attributed to peculiarities of interaction of this rubber with industrial carbon P324. Figure 1; references 6 (Russian).

Study of Strength of Rubbers With Different Content of Ground Vulcanizate

[Article by V. A. Zubov, A. B. Vetoshkin and S. V. Usachev]

UDC 678.033-492.2.35

[Abstract] A study of the effect of the sulfur/accelarator ratio on the properties of different rubbers determined the effect of doses of vulcanizates on the tensile strength of rubbers with 6 percent and 12 percent of ground vulcanizate. The presence of 6 percent ground vulcanizate required an increase of dosing of sulfur and a decrease of the accelator level while the presence of 12 percent ground vulcanizate required the opposite procedure. Production of composites with higher tensile strength called for an increase of either sulfur or accelerator according to the ground vulcanizate level. High strength of rubbers with a low content of ground vulcanizate in them may be achieved because of formation around the ground vulcanizate particles of more developed layers of the matrix with a reduced degree of crosslinking. A ground vulcanizate level of more than 10 percent produced a tendency to a decrease of the extent of low-modular layers around particles of the dispersed phase. Figure 1; references 5 (Russian).

Increase of Resistance of Rubbers Based on Combination of Raw Rubbers

[Article A. F. Puchkov and A. M. Ogrel]

UDC 678.4.063

[Abstract] Examination of a filled elastomer composition based on SKMS-30ARKM-15 and SKI-3 with rubber mixtures prepared on laboratory rollers showed that the durability level of the vulcanizates, under thermooxidative conditions, depend upon which of the rubbers receive the anti-ager and upon the fraction of this rubber in the elastomer matrix. Microphotographs of initial vulcanizates and those based on a polyisoprene-polybutadiene combination mixture prepared by ordinary methods and prepared in butadiene rubber with preliminary introduction of the anti-ager showed that, after thermooxidative aging at 70 degrees C for 7 days, showed the greatest contrast of microstructure in the 1st sample while the microstructure of the 2d was practically unchanged. After aging under these conditions, K_{fp} was 0.54 for sample 1 and 0.95 for sample 2. Thus, the studies showed that preliminary treatment of the anti-ager or groups of anti-agers with one of the rubbers of the combination increases the stability of rubbers, subjected to thermooxidation aging, 1.1-1.5 times in strength and 1.1-1.6 times in relative elongation. Figures 2; references 3 (Russian).

Dependence of Properties of Thermoelastoplasts on Composition and Structure

[Article by A. N. Kondratyev and Ye. F. Mironova]

UDC 678.074.01

[Abstract] A method developed by the authors made it possible to determine the factors upon which M_s (molecular mass of chains between crosslinkings) depend and how it affects the properties of thermoelastoplasts. Determination of M_s for thermoelastoplasts with linear and branched structure with the same proportion of the rigid phase showed that M_s in branched thermoelastoplasts is higher than that in linear thermoelastoplasts. It was shown that the properties of thermoelastoplasts depend basically on the ratio of monomers and the size of the interphase layer. Figure 1; references 4 (Russian).

Effect of Microorganisms on Protective Properties of Anticorrosion Coatings Based on Polysulfide Sealants

[Article by T. S. Onishchenko, A. S. Kostin and Ye. I. Bordukova]

UDC 576.8:629.73-036.8

[Abstract] Assessment of the corrosiveness of microscopic fungi relative to polysulfide sealants involved a

study of free films of sealants U-30MES-5, U-30MES-5M and VTK-1-29. Samples of the sealants in 100x25x(1.5 + or - 0.5) mm plates were soaked in kerosene for 35 hours, dried at 25 +/- 2°C and relative humidity of 75 +/- 5 percent for 72 hours. They were then exposed for 11 months in a 2-phase mineral-fuel medium infected by spores of the microscopic fungus Cladosporium resinae. The microrganisms developing in the petroleum distillate fuels decreased the anticorrosion properties of the polysulfide coatings. They changed the sealant structure and diminished their protective properties. The findings made possible a quantitative assessment of corrosiveness of the microorganims and the biostability of the polysulfide sealants. Figure 1; references 5 (Russian).

Hardening of Urethane-epoxy Rubber by Amine

927M0008F Moscow KAUCHUK I REZINA in Russian No 6, June 1991 pp 30-32

[Article by A. B. Korennaya, T. P. Nasonova, S. A. Bogatyreva and V. F. Kuznetsova]

UDC 678.664:678.028:533,534

[Abstract] A study of reactions proceeding during reaction for 168 hours at 80°C of oligodieneurethane-epoxy with aniline at an equimolar ratio of amine/epoxy equal to 0.72, 0.36 and 0.22 (compositions 1, 2, 3) used gas-liquid chromatography to study formation of monohydroxyaniline and to calculate values of the rate constant of reactions of the 1st and 2d order. Infra-red spectroscopy produced data concerning expenditure of epoxy-groups, the level of forming hydroxyl groups and products of cyclization. This procedure revealed a group of reactions in the oligo-dieneurethane-epoxy-aniline system and permitted assessment of the percent of each reaction as a function of the time of hardening and the quantity of aniline. The dihydroxy-aniline formation reaction, leading to elongation of the chain, proceeded only partially with the increase of the quantity of aniline. Branching of the chains occurred because of interaction of the OH-groups of hydroxyaniline with the epoxyurethane, the percent of which increased with the increase of aniline level. The rate of formation of monohydroxyaniline conformed to the passage of reactions within the limits of the polar associates. The change of molecular-mass characteristics, determined by gas-lquid chromatography, and the gel level in the compositions correlated with processes leading to elongation and branching of the macromolecules. References 8 (Russian).

Modification of 2,4-Toluylenediisocyanate and Methyl Methacrylate Polymeric Glasses with Urethane Oligomers Having Terminal Unsaturated Groups

927M0034A Moscow PLASTICHESKIYE MASSY in Russian No 6, Jun 91 pp 11-12

[Article by V. N. Nikolayev and M. M. Izheyeva]

UDC678.744.335-135.462.682.001.73

[Abstract] Vinyl monomers may be copolymerized with 2,4- toluylenediisocyanate (TDI) in the presence of an anionic catalyst to form a brittle polymer glass. In the present work the possibility of using urethane oligomers having terminal unsaturated groups to prepare impact-resistant polymer glasses was explored. TDI was copolymerized with methyl methacrylate (MMA) in the presence of urethane oligomers having allyl and methacrylic terminal groups. Block copolymerization of the above at 25°C results in formation of a copolymer having a gel fraction containing 99 percent brittle glass having an impact resilience of 3.0 kJoules/m². On introduction of various types of urethane oligomers the curing time of the composition and the quality of the polymer glasses vary. Evidently the urethane oligomers act both as grafting agents and elasticizers to raise the impact resilience of the resulting polymer glasses. Figures 2; references 5 (Russian).

Thermomechanical Properties of PVC, Filled with Crude Lignin

927M0034B Moscow PLASTICHESKIYE MASSY in Russian No 6, Jun 91 pp 17-18

[Article by E. R. Galimov, R. K. Nizamov, and V. P. Dmitriyev

UDC678.743.22:547.992.3:536.6

[Abstract] The technological and service characteristics of materials may be evaluated from the thermomechanical properties of the polymers from which they are made. A study was made of the effect crude lignin type has on the thermomechanical properties of rigid and plasticized polyvinyl chloride (PVC). Modifiers consisted of waste hydrolysis lignin, "karamel" (multi-ton waste from yeast production), and cellulose-paper sludge. The resulting data demonstrates that introduction of crude lignin to PVC compositions has practically no effect on the temperature range at which it is used, since the glassification temperature changes very little. However, the tensile strength of rigid products containing 30 and 50 parts by weight of dioctyl phthalate increases with addition of crude lignin. At low crude lignin dosages, the flow point temperature of rigid and mildly plasticized PVC compositions is markedly lower, thereby facilitating working these compositions at lower temperatures. Figures 2; references 13 (Russian).

Temperature Dependence of Electrical Properties of PUF, Painted with Conducting Enamel

927M0034C Moscow PLASTICHESKIYE MASSY in Russian No 6, Jun 91 pp 20-21

[Article by G. G. Petrzhik, S. N. Nazin, and V. A. Ogarev]

UDC678.664-405.01:537.226:536.6

[Abstract] In a previous work it was demonstrated that pigmenting the entire open pore surface of polyurethane foam (PUF) with a conducting type enamel (KhP-5237) based on a hydrocarbon filler and chlorosulfonated polyethylene results in a three-dimensional network within the PUF bulk. The conducting network is highly polarized from the polarization of the individual carbon particles and their aggregates, as well as from the charges on the microcondensors formed by PUF membranes which have a conductive coating on both sides. Temperature dependence of electrophysical properties of composite materials filled with carbon and graphite are determined by the filler content, the polymer type, surface structure of the filler particles, and the distribution of the latter within the bulk. Temperature effects thus provide significant information on the conducting structure and the nature of the contacts between filler particles. These data are also needed to establish the service characteristics of conducting composites. In the present work a study was made of the changes in effective dielectric permeability and specific active conductance in alternating current passed through pigmented PUF over the frequency range 10 Hz to 100 MHz and 50° to 70° C. In addition to active conductance, the elastic enamel also has a large bulk reactive component in the electrical current over a wide frequency range. The magnitude of the latter (at low frequencies) is evidently the result of charges on the microcondensors formed within the bulk of the porous structure membranes during painting, and (at high frequencies) by polarization of aggregates and individual particles of the conductive pigment. Electrophysical parameters change little with temperature over the range studied. Increasing the quantity of conductive pigment raises both the active and reactive conductance of painted PUF over the entire frequency range. Figures 2; references 5: 3 Russian, 2 Western.

Lowering the Rate of Oxidative Breakdown of PVB

927M0034D Moscow PLASTICHESKIYE MASSY in Russian No 6, Jun 91 pp 42-43

[Article by M. A. Mkhitaryan, T. V. Monakhova, P. S. Voskanyan, and A. P. Marin]

UDC678.744.534.019.31:66.094.3

[Abstract] Polyvinyl butyral (PVB) is a condensation product of polyvinyl alcohol and butyraldehyde that is widely used in shatter-proof glass as a component containing a plasticizer and stabilizers. High transparency and stability in service are basic requirements. One cause for deterioration in optical properties lies in the appearance of coloration in the product during processing at high temperatures. At temperatures above 150° C and the absence of oxygen, PVB rapidly decomposes into butyraldehyde and water. In the presence of oxygen, PVB decomposition is accelerated, thereby increasing the yield of gaseous products and formation of non-volatile oxygen-containing products, including hydroperoxides. It has been demonstrated that the basic cause of PVB yellowing is the breakdown of hydroperoxide groups to form conjugated double bonds and carbonyl groups joined to the double bonds. A linear relationship was established between the degree of yellowing and the hydroperoxide content in the initial polymer. In the present work oxidation of PVB in the presence of antioxidants was studied for the purpose of developing compositions having high optical qualities. Addition of a phenolic type antioxidant (Fenozan-28) and mixtures thereof with phosphites makes it possible to prepare an adhesive laminate for single-layer glasses which do not yellow during processing at temperatures up to 180° C. Figures 2; references 4 (Russian).

New Developments in Extrusion Technology of Composite Materials

927M0034E Moscow PLASTICHESKIYE MASSY in Russian No 6, Jun 91 pp 46-47

[Article by E. L. Kalinchev and A. Yu. Melnikov]

UDC678.027.3

[Abstract] Pressure casting and extrusion are frequently used in handling thermo-plastics in the viscous flow state. Material flow is initiated by pressure created within the equipment. The nature of the flow, steadiness in rate, and energy consumed are functions of the relation of flow resistance to applied pressure conditions. In pressure casting there are two sets of conditions: 1) constant flow rate, and 2) diminishing flow rate. Set 1 is determined by the equipment parameters, making it is possible to regulate and maintain process speed at a required level. Set 2 is a function of the equipment parameters, precluding the possibility of process control. Study of extrusion processes for various composite materials and pure polymers also revealed two areas. The first area is that of stable extruder operation as estimated by worm feeder rotation, where it is possible to regulate and maintain process parameters. The second area, that of unstable extruder operation and also estimated by worm feeder rotation, is characterized by a drop in work stability with changes in parameters affecting turning moment, temperature, pressure, etc. An extruder designed for composite materials to provide mixing, de-gassing, and other processes must be long (up to 40 inches). In the event of minor fluctuations in extrusion parameters, the maximum value of the turning moment may be exceeded and lead to overloading and damage to the costly worm feeders. For this reason, a blocking system must be used to control the turning moment and make it possible to conduct the process in the first area to prevent extruder stoppages during short-term overloading. Figure 1.

Optimization of Reaction for Preparation of Benzylamine Modified Phenolformaldehyde Resin

927M0035A Moscow PLASTICHESKIYE MASSY in Russian No 7, Jul 91 pp 3-4

[Article by R. P. Dzhafarov, Ya. G. Abdullayev, Kh. A. Salayeva, F. T. Aliyev, S. M. Akhmedov, and F. M. Abdurakhmanova]

UDC678.632'32'21.001.73:66.091

The physical mechanical characteristics of phenolformaldehyde materials may be significantly improved through chemical modification of the initial phenolformaldehyde oligomers. Modification of the oligomers during the phenol- formaldehyde stage with nitrogen-containing compounds is one of the most promising ways to synthesize new types of phenolformaldehyde oligomers having good service properties. The synthesis is usually carried out by condensation of phenol, formaldehyde, and the nitrogen-containing compound in acid media. In the present work a mathematical model developed for optimizing the reaction, indicates that the optimal entering variables are: 1 : 0.1 phenol : benzylamine ratio, 95° C temperature, and 3.2 hours reaction time to give maximum yield and viscosity. Figure 1; references 5 (Russian).

Progressive Technology for Preparing Prepregs for Reinforced Plastics with Thermo-reactive Binders

927M0035B Moscow PLASTICHESKIYE MASSY in Russian No 7, Jul 91 pp 7-10

[Article by M. S. Trizno, Ye. A. Stenshinskaya, and V. N. Leontyev]

UDC678.026.2.029.46:620.22-419.8

[Abstract] Reinforced plastics using thermo-reactive binders are used widely. At the present time the most progressive technology for fabricating reinforced plastic products involves pre-finished products, particularly prepregs. Prepregs consist of continuous-formed reinforcing fillers, such as tapes or fabric rolls which are pre-impregnated with a binder. They are most frequently produced by impregnating the reinforcing filler with the binder in organic solvents in horizontal or vertical drying machines. However, this technology has many drawbacks related to elimination of the solvent. A new ecologically safe "solvent- free" technology which impregnates the filler with a thermo- reactive plastic in the molten state in a rolling mill is presented. Figure 1; references 11 (Russian).

Properties of Caprolactam-Dodecalactam Block Copolymers

927M0035B Moscow PLASTICHESKIYE MASSY inRussianNo 7, Jul 91 pp 12-14

[Article by Ye. G. Rayevskaya, Ye. S. Artsis, N. P. Bessonova, I. V. Ivankina, and M. I. Siling]

UDC678.675-13.01

[Abstract] The preparation of materials having the combined properties of PA-6 and PA-12 polyamides has great practical significance because these polyamides elastic are both water and frost resistant. A block copolyamide of ε-caprolactam and o-dodecalactam was synthesized in a previous work. In the present work a determination of the physical, mechanical, and other properties of this copolymer demonstrates that it is equivalent in properties to PA-6 and PA-12 polyamides. Figures 3; references 8: 6 Russian, 2 Western.

Interrelationship of Structural and Diffusion-Kinetic Processes Taking Place in Polymers Having Varying Degrees of Hydrophily

927M0035D Moscow PLASTICHESKIYE MASSY in Russian No 7, Jul 91 pp 25-30

[Article by A. L. Iordanskiy, A. Ya. Polishchuk, R. Yu. Kosenko, N. N. Madyuskin, O. V. Shatalova, L. L. Razumova, and G. Ye. Zaikov]

UDC678.01:539.2:66.063.2

[Abstract] Both theory and practice of utilizing membrane technology are based on studying diffusion phenomena since it is chiefly the latter that determines the mechanisms of separation, purification, and concentration of electrolytes using polymer membranes. Insufficient study of the interrelationship between polymer structure and the kinetics of diffusion processes in materials having varying degrees of hydrophily hinders the evaluation and prediction of behavior in diffusion systems whose structure is apt to change with time (dialysis systems, medicinal storage, and membrane sensors for monitoring the status of the environment). In the present work a quantitative analysis was made of the diffusion of aqueous solutions of electrolytes through hydrophilic (polyvinyl alcohol) and moderately hydrophilic (PA-6 and PA-6.6 polyamides). Film structure in the dry and wet states was studied using X-ray diffractometry and a specially designed device was used to study permeation of water and aqueous solutions of organic and inorganic acids through the membrane films. A model simulating the diffusion processes is presented which may be used to explain the transport basics of mineral acids in PA-6, describe the kinetics of structural changes, and calculate the parameters characterizing the properties of water-polymer systems. Figures 5; references 24: 14 Russian, 10 Western.

Long Term Durability of Polymers in Liquid Media

927M0035E Moscow PLASTICHESKIYE MASSY in Russian No 7, Jul 91 p 34

[Article by G. A. Serebryakov, S. Sitamov, V. M. Aristov, A. I. Khukmatov]

UDC678.7:620.172

[Abstract] Long term durability of polymers in liquid media under equal conditions is determined by the rate of diffusion into the polymer. In a previous study of long term durability of polymers in various media it was demonstrated that time is a function of pressure. For polymers stored in air over a broad range of temperatures and pressures the function is linear; in liquids it is non-linear. A relationship for depth of penetration of water into high impact polystyrene as a function of diffusion is also presented. By using Fourier's coefficient in evaluating long term durability of polymers it is possible to correlate the diffusion of a liquid medium into a polymer with the thickness of the material and the time it is kept in a corrosive medium. Figure 1; references 2 (Russian).

Adhesive Covering Made of Polyethylene

[Article by S. Sh. Saytiyev]

UDC678.742.2.049.16

[Abstract] Composite anticorrosive material MKA consists of a rolled laminate covering having a polyethylene base on which glass fabric or paper is applied by heat press. The covering is made in two forms, depending on the arrangement of layers at the Ufa NIIpromstroy (TU 65.313-82). The covering, being a multi- layer laminate with each layer having positive properties in combination with the other layers, is said to have high strength and heat resistance. It is flexible and may be applied with bituminous mastic, adhesive 88-N, or epoxy glue to wood, stone, concrete or metal surfaces. A non-adhesive method for securing the covering to reinforced concrete objects such as building panels, conduits, boats, canals, etc. has been developed. The covering is used in construction as an independent waterproofing material and as insulation in chemically resistant flooring. The large size of the rolls (90-100 cm wide, 50 meters long) reduces the number of seams. Figure 1.

Effect of Multiple Reprocessing on Properties of Highly Filled High Density Polyethylene

[Article by I. I. Fatoyev, D. Nazarov, and S. Sitamov]

UDC678.742.23.033.027

[Abstract] Although polyethylene is produced in great quantities and is one of the most widely distributed polymers, it is still in short supply. Presently, the demand for polyethylene is only 55 percent satisfied. As the volume of recycled polyethylene increases, the need for utilizing scrap polyethylene arises. Since the properties of non-filled polyethylene after multiple reprocessing are well known, a study was made of the effects of multiple reprocessing on high density high filled polyethylene. Data are presented on 1 to 7 reprocessing cycles listing changes in density, tensile strength, relative elongation to rupture, elasticity modulus, impact resilience, Brinell hardness, and coefficient of permeability. By changing the multiplicity of reprocessing high filled polymer composite materials it is possible to regulate the microstructure of these materials and improve their diffusion characteristics. References 6 (Russian).

The Dynamics of Electron Tracks in Liquid Water

[Article by A.V. Ponomarev, I.Ye. Makarov, and A.K. Pikayev, Physical Chemistry Institute, USSR Academy of Sciences]

UDC 541.15

[Abstract] The authors of the study reported herein used the Monte Carlo method to model the occurrence of a fast-electron track, the dynamics of the spatial distribution of radiolysis products in the physical and physicochemical states, and the noninstantaneous kinetics of intratrack chemical reactions in irradiated liquid water. Unlike previous research on the said topic, the present examination gives consideration to the plurality of water molecule ionization channels, uses data regarding the lengths of the electrons' and molecular ions' thermalization, and allows for the characteristic features of the spatial distribution of excited states. Specifically, they modeled the spatial distribution of electron activations and the subsequent spatial distribution to the thermalized primary decay products in an electron track with an energy of 1 MeV in liquid water at room temperature. Consideration was given to the five stages of ionization and the formation of five excited singlet states of the water and collective excited plasma-type states in the physical stage of radiolysis. The yields of the ion and radical pairs before the chemical reactions were as follows (pairs/100 eV): e^--H_2O^+, 5.24; OH-H, 1.98; and H_2-O, 0.77. The yields of the water radiolysis products after the study reactions were completed were as follows (pairs/100 eV): e_{aq}, 2.92; H_3O^+, 3.5; OH, 3.02; H, 0.64; H_2O_2, 0.73; H_2, 0.46; and OH^-, 0.58. The authors note that the initial electron, oppositely charged ion, and OH radical yields calculated herein are lower than those published elsewhere. They attribute this difference to the role of the high-energy ionization channels in liquid water, which were not given consideration when the previously published values were calculated. They propose that future calculations include an estimation of the role of the plurality of hole states and spin effects during ion-electron recombination in irradiated liquid water. Figures 3, tables 7; references 18: 9 Russian, 9 Western.

Characteristic Features of the Effects of γ-Radiation and α-Particles on Polyvinylidene Fluoride

[Article by B.K. Pasakalskiy, D.A. Sachuk, L.N. Grebinskaya, and Ya.I. Lavrentovich, Physical Chemistry Institute imeni L.V. Pisarzhevskiy, UkSSR Academy of Sciences]

UDC 541.64+678

[Abstract] The authors of the study reported herein examined the effect of γ-^{60}Co and α-particles on polyvinylidene fluoride. Specifically, they studied the nature of the formation and thermal destruction of paramagnetic centers, as well as the process of the cross-linking of macromolecules in polyvinylidene fluoride irradiated by radiation with different transmission energies. For the studies, the authors used polyvinylidene fluoride (density, 1.75 g/cm^3) that did not contain any extraneous impurities. The polyvinylidene fluoride used was in the form of films 200 μm thick. The films were irradiated with ^{60}Co γ-radiation and α-particles with an energy of 22 MeV in a vacuum of about 10^{-3} Pa at the boiling point of nitrogen. The linear transmission energy was varied from 0.2 to 50 keV/μm. The experiments revealed that varying the linear transmission energy within the said limits does not affect the nature of polyvinylidene fluorides stabilized at 77 K. Nor does it affect their thermal decomposition kinetics or their gel fraction content after irradiation. The total yield of polyvinylidene fluorides was, however, found to decrease as the linear transmission energy increased. This was linked to the destruction of some radicals directly in the α-particle tracks on account of local heating of the space around the track that occurs in the primary stages of radiolysis (even at low temperatures). Figures 2; references 6: 4 Russian, 2 Western.

Effect of Temperature on Radiolysis of Di-2-Ethylhexylsebacinate

[Article by N.S. Oreshkova, V.V. Sarayeva, and M.F. Romantsev, Moscow State University imeni M.V. Lomonosov]

UDC 541.15

[Abstract] The authors of the study reported herein examined the kinetics of the accumulation of products of the radiolysis of di-2-ethylhexylsebacinate during irradiation at different temperatures. They subjected commercial-grade di-2-ethylhexylsebacinate to purification on activated aluminum oxide. Specimens of the purified di-2-ethylhexylsebacinate were deaerated by repeated freezing by liquid nitrogen to a residual pressure of 0.013 Pa and then irradiated in glass ampules. ^{60}Co was used as an ionizing radiation source. A dose rate of 13 Gy/s was used. The degree of radiolytic transformation of the di-2-ethylhexylsebacinate, its content, and its radiolysis products were determined chromatographically by a method detailed elsewhere. The effect of temperature on the transformation of di-2-ethylhexylsebacinate at 320-470 K was studied in the dose interval from 0.01 to 1.00 MGy. Because the dependence of the degree of di-2-ethylhexylsebacinate transformation on radiation dose is nonlinear, the decomposition yield was calculated

from the initial segments of the kinetic curves. At 320 K (with a dose up to 0.05 MGy), the yield equaled 9.0 +/- 2.0 molecules per 100 eV; at 400 K, the yield amounted to 19.7 +/- 4.3 molecules per 100 eV; and at 470 K, it amounted to 81.3 +/- 6.9 molecules per 100 eV. The yields of 2-ethylhexene and hydrogen were found to be virtually independent of temperature in the interval between 320 and 470 K. The yields of carbon dioxide, 2-ethylhexylpelargonate, butyric aldehyde, heptane, and high-boiling components were found to increase slightly in the temperature interval from 320 to 400 K; a strong increase in their yields was observed at temperatures above 400 K. The yields of carbon monoxide and acidic products were found to increase in a linear manner as the temperature increased, whereas the yield of 2-ethylhexanol was observed to decrease as the temperature was increased. The authors conclude by stating that research on the effect of acceptors may provide a more complete understanding of the ways in which the various aforesaid radiolysis products are formed. Figures 2, table 1; references 5 (Russian).

The Radiolysis of Tetrazolium Salts in Polyvinyl Alcohol

[Article by Z.K. Zriminskaya, S.F. Ginzburg, and A.A. Molin, Organic Intermediate Products and Dyes Scientific Research Institute]

UDC 541.15

[Abstract] The authors of the study reported herein measured the radiochemical yields of formazanes in binary systems containing polyvinyl alcohol and tetrazolium salts as additives. For their experiments the authors used graded-for-analysis 2,3,5-triphenyltetrazolium chloride [TTC], 2-n-nitrophenyl-3,5-diphenyltetrazolium chloride [n-NTC] (manufactured by the firm Reanal), and 18/11 polyvinyl alcohol. Aqueous (in the case of TTC) or alcohol (in the case of n-NTC) solutions of varying concentrations of tetrazolium salt were added to an 8% hot aqueous solution of polyvinyl alcohol. The resultant homogeneous transparent solutions were poured into Petri dishes and dried at room temperature for several days. The result in each case was a transparent pale yellow film 0.1 to 0.15 mm thick. The films were cut into rectangular wafers measuring 4 x 1.5 cm and subjected to irradiation at a dose of 1.6 Gy/s. Plane films 3-3.5 and 7-8 mm wide and 8-12 cm long were used for the low-temperature radiolysis. Their EPR spectra were measured at various points in the temperature interval from 120 to 220 K. Analysis of the measurements taken indicated that the radiochemical yield of formazanes [G(F)], which are a product of the two-electron reduction of tetrazolium salts, exceed one-half the radiochemical yield of radicals in polyvinyl

alcohol $[1/2G_{rad}]$. In the case of high n-NTC concentrations, the yield is greater than $1/2G_{rad}$ by more than a factor of 2. The only exception occurs in the case of polyvinyl alcohol films containing TTC in the amount of 7.4×10^{-3} mol/l, where G(F) = 0.86. This fact leads the authors to speculate that the mechanism of the effect of radiation in the given case depends both on the distance between the matrix radical and salt molecule and on the salt's acceptor properties. The different EPR spectra observed at 77, 120, and 200 K are analyzed. The authors hypothesize that the increase in the concentration of single radicals at temperatures above 400 K is due to the participation of radical pairs in the reaction. The authors conclude by stating that the fact that the radiochemical reduction yield in polyvinyl alcohol surpasses the yield of free radicals may be explained by the activation of acceptors in the radical pairs. Figures 4, table 1; references 15: 6 Russian, 9 Western.

The Effect of Different Types of Ionizing Radiations on the Properties of Polymers. Radiation-Induced Electric Conduction

[Article by A.P. Tyutnev, V.P. Sichkar, and S.G. Boyev, Physical Chemistry Scientific Research Institute imeni L.Ya. Karpov and Tomsk Polytechnic Institute imeni S.M. Kirov]

UDC 541.15:539.2

[Abstract] The authors of the study reported herein compared the electric conduction of low-density polyethylene and polystyrene induced by different types of irradiation. Specifically, they compared the electric conduction induced by continuous-wave γ-^{60}Co radiation, protons accelerated to an energy of 7.7 MeV, and α-particles with an energy of 20 MeV. During the measurements of radiation-induced electric conduction, the absorbed dose did not exceed 2 kGy in the case of the γ-radiation, 5 kGy in the case of the protons, and 8 Gy in the case of the α-particles. A regular decrease in radiation-induced electric conduction was observed in the series γ-^{60}Co irradiation, accelerated proton irradiation, and α-particle irradiation per unit dose rate. The pattern observed was found to be in good agreement with previously published measurements of track effects in nonstationary induced electric conduction when specimens were irradiated by pulses of electrons, protons, and α-particles for 0.3 to 3.6 ms. The amount of radiation-induced electric conduction in both polystyrene and low-pressure polyethylene, in particular, the marked increase in the track effect upon the transition from nonstationary induced electric conduction to radiation-induced electric conduction, is discussed in terms of the scientific literature and the experiment reported herein. The authors conclude that the significant differences in the radiation-induced electric conduction of polymers

irradiated by the aforesaid different types of ionizing radiation are linked with the rapid recombination of charge carriers in isolated tracks. They state that this recombination increases as the linear transmission energy of the radiation increases. They did not, however, observe any direct dependence between the increase in linear transmission energy and decrease in radiation-induced electric conduction. They account for this fact by stating that the track effects in this case should indeed be less pronounced because of the asymptotic form of the law of bimolecular recombination in this specific case (according to which, the drop in concentration over time does not depend on the initial concentration of charge carriers. Figure 1, table 1; references 7 (Russian).

Radiochemical Processes in Polymer Films Containing N,N,N',N'-Tetramethyl-4,4'-Diaminodiphenylmethane Under the Effect of Pulses of Accelerated Electrons

[Article by A.S. Kolotilkin, V.A. Tkachev, Ye.I. Maltsev, and A.V. Vannikov, Electrochemistry Institute imeni A.N. Frumkin, USSR Academy of Sciences]

UDC 541.15

[Abstract] The authors of the study reported herein examined the early stages of the radiochemical oxidation of N,N,N',N'-tetramethyl-4,4'-diaminodiphenyl-methane [TMDH] in solid solutions of polyvinyl chloride and polymethyl methacrylate in the presence and absence of the electron acceptor CBr_4. As polymer binders, the researchers used polyvinyl chloride [PVC] and polymethyl methacrylate [PMMA] that were free of extraneous additives. The study was based on the pulsed radiolysis method. An Elektronika 003 linear electron accelerator capable of sending single pulses lasting 5 μs and equipped with a system for optical recording of colored radiolysis products was used as the ionizing radiation source. A current of 1 A was used in the pulse, the per-pulse dose amounted to 9 x 10^2 Gy, and the electron energy amounted to 4 MeV. The study specimen was placed at a 45° angle to the beam of accelerated electrons and the analyzing luminous flux. The researchers recording the absorption spectra and identified the short-lived radiolysis products of TMDH. They also determined the radiochemical yields and calculated the rate constants of the reactions of the formation of the stable colored radiolysis product Michler's hydrol. The rate constants for the systems PVC-TMDH-CBr_4 and PMMA-TMDH-CBr_4 equaled 240 +/- 25 and 20 +/- 3 s^{-1}, respectively. On the basis of data taken from the literature and from their own experiments reported herein, the authors present 15 equations describing the radiochemical oxidation of TMDH both in the presence and absence of the acceptor CBr_4 in PVC films. The scheme presented for the case where CBr_4 is present makes an

allowance for the effect of radiation on the CBr_4 and TMDH because the electron fraction of these substances in the polymer matrix at a concentration of 0.9 mol/dm³ amounts to 15 and 14%, respectively. Figures 3, table 1; references 15: 10 Russian, 5 Western.

Radicals in γ-Irradiated Wool

[Article by N.N. Bayeva, S.F. Sadova, and V.A. Sharpa-tyy, Chemical Physics Institute, USSR Academy of Sciences]

UDC 577.391,535.37,541.15

[Abstract] The primary objective of the study reported herein was to determine the main types of radicals recorded by the EPR method during the low-temperature irradiation of wool and to estimate their partial yield. As their study object the researchers selected 64 K merino wool fiber, a natural product whose morphology, structural properties, and amino acid makeup have all been comparatively well studied. Specimens of the wool with a greater-than-99% protein content were cleaned, dried to a constant mass at 360 K, and placed in glass ampules that did not give off a noticeable EPR signal after irradiation. They ampules were evacuated, filled with argon, and sealed. The specimens were irradiated in liquid nitrogen on a radioactive cobalt device in the dose interval from 10 to 180 kGy. The EPR spectra of the irradiated wool specimens were recorded, and their concentration of radicals was measured on a type EPR-V spectrometer in accordance with the generally accepted method. Seven free radicals were identified on the basis of EPR spectra of wool specimens subjected to ^{60}Co γ-irradiation at 77 K. The accumulation of radicals during the course of irradiation observed during the experiment followed the typical dependence for accumulation during low-temperature irradiation of biopolymers, dry preparations, and frozen solutions: $C(\Sigma R) = C_\infty(1 - \exp[-kD])$, where C_∞ is the concentration of radicals recorded at high radiation doses (D) and k is the rate constant of the radicals' destruction directly during the irradiation. The total concentration of radical in the specimens decreased as they were heated. The temperature intervals corresponding to the stability of the given radicals are presented in table form along with the proposed structures and formation reactions of the given radicals and other pertinent data. After comparing the shapes of the EPR spectra of wool and other protein specimens irradiated under identical conditions the authors concluded that the observed differences in the spectra of the two materials (wool versus protein) could be explained by the nonidentical values of the partial yield of the macroradicals formed in the irradiated proteins as a result of the occurrence of a single type of primary process, i.e., during the interaction of the electron (e) and atom (H) with the individual amino acid

residues in the macromolecules and carbo groups of the peptide chains (pc), as well as during the splitting of the C_α-H bonds in the polypeptide chain. In view of the partial yields obtained for the processes involving the electron (e), the scale of its reactivity with respect to those fragments of the protein molecule attacked by it in wool irradiated at 77 K was said to be as follows: [RSSR]:[>C=O$_{pc}$]:[NH$_3^+$-R]:[aromatic rings]=4:3>1:1. Figure 1, table 1; references 10: 7 Russian, 3 Western.

Transformations of the Free Radicals of a DNA Sugar Fragment During Radiolysis

[Article by A.T. Koritskiy and V.A. Sharpatyy, Chemical Physics Institute, USSR Academy of Sciences]

UDC 541.15+541.515+577.391

[Abstract] The authors of this article examine the problem of the role of the primary radicals of the sugar fragment of DNA in the formation of alkaline-labile sites in the polymer during the γ-irradiation of DNA and cells. They base their analysis on data from their own research and that of other investigators. They draw a number of conclusions regarding the transformation mechanism resulting in the formation of four end products, namely, modified sugars in the makeup of DNA that are labile to the effect of alkali and can be recorded by various methods. The first of the four radiolysis products discussed is said to form as a result of damage in the nucleotide of the nitrous base. OH-, e-, and H-adducts of the bases form under the effect of radicals that are products of the radiolysis of water. They undergo a transformation process that entails the formation of compounds with saturated bonds that eventually result in the hydrolysis of the N-C' bonds and in the appearance of the first of the four modified sugar fragments discussed. The second, third, and fourth radiolysis products examined are said to be associated with the initial damage in the nucleotides of the fragment 2-deoxyribose. In other words, they are associated with transformations of the primary macroradicals involving the localization of the free valence on the sugar link. Product 2 is recorded only when DNA is irradiated in the presence of O_2. The occurrence of product 2 may thus be linked to the formation and transformation of a peroxide radical of the C_2OO type. Products 3 and 4 contain a carbonyl group. The authors hypothesize that both these products are formed in the same type of reaction of the transformation of radicals, with the free valence localized on the carbon atom (on the primary carbon atom [C_1'] in the case of product 3 and on the secondary atom [HC_1'] in the in the case of product 4). A hydrolytic splitting of the C_1'-N bond resulting in the carbonyl group C_1=O is said to occur in both these radicals. The authors also discuss evidence in favor of the possible transfer of the free valence from the sugar fragment to the DNA base. Figures 2; references 13: 6 Russian, 7 Western.

NTIS
ATTN PROCESS 103

2

5285 PORT ROYAL RD
SPRINGFIELD VA

22161

Foreign Broadcast Information Service (FBIS) and Joint Publications Research Service (JPRS) publications contain political, military, economic, environmental, and sociological news, commentary, and other information, as well as scientific and technical data and reports. All information has been obtained from foreign radio and television broadcasts, news agency transmissions, newspapers, books, and periodicals. Items generally are processed from the first or best available sources. It should not be inferred that they have been disseminated only in the medium, in the language, or to the area indicated. Items from foreign language sources are translated; those from English-language sources are transcribed. Except for excluding certain diacritics, FBIS renders personal names and place-names in accordance with the romanization systems approved for U.S. Government publications by the U.S. Board of Geographic Names.

Headlines, editorial reports, and material enclosed in brackets [ ] are supplied by FBIS/JPRS. Processing indicators such as [Text] or [Excerpts] in the first line of each item indicate how the information was processed from the original. Unfamiliar names rendered phonetically are enclosed in parentheses. Words or names preceded by a question mark and enclosed in parentheses were not clear from the original source but have been supplied as appropriate to the context. Other unattributed parenthetical notes within the body of an item originate with the source. Times within items are as given by the source. Passages in boldface or italics are as published.

SUBSCRIPTION/PROCUREMENT INFORMATION

The FBIS DAILY REPORT contains current news and information and is published Monday through Friday in eight volumes: China, East Europe, Central Eurasia, East Asia, Near East & South Asia, Sub-Saharan Africa, Latin America, and West Europe. Supplements to the DAILY REPORTs may also be available periodically and will be distributed to regular DAILY REPORT subscribers. JPRS publications, which include approximately 50 regional, worldwide, and topical reports, generally contain less time-sensitive information and are published periodically.

Current DAILY REPORTs and JPRS publications are listed in *Government Reports Announcements* issued semimonthly by the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22161 and the *Monthly Catalog of U.S. Government Publications* issued by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

The public may subscribe to either hardcover or microfiche versions of the DAILY REPORTs and JPRS publications through NTIS at the above address or by calling (703) 487-4630. Subscription rates will be provided by NTIS upon request. Subscriptions are available outside the United States from NTIS or appointed foreign dealers. New subscribers should expect a 30-day delay in receipt of the first issue.

U.S. Government offices may obtain subscriptions to the DAILY REPORTs or JPRS publications (hardcover or microfiche) at no charge through their sponsoring organizations. For additional information or assistance, call FBIS, (202) 338-6735,or write to P.O. Box 2604, Washington, D.C. 20013. Department of Defense consumers are required to submit requests through appropriate command validation channels to DIA, RTS-2C, Washington, D.C. 20301. (Telephone: (202) 373-3771, Autovon: 243-3771.)

Back issues or single copies of the DAILY REPORTs and JPRS publications are not available. Both the DAILY REPORTs and the JPRS publications are on file for public reference at the Library of Congress and at many Federal Depository Libraries. Reference copies may also be seen at many public and university libraries throughout the United States.